VISIT…

Appendix

ANSWERS TO IN-CHAPTER PROBLEMS

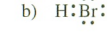
Answers to selected in-chapter problems are provided in this appendix. Complete answers to all of the problems can be found in the Solutions Manual that accompanies this text.

CHAPTER 1

1.1 a) $:\ddot{\underset{\cdot\cdot}{Br}}\cdot$ b) $\cdot Ca\cdot$ c) $\cdot\dot{\underset{\cdot\cdot}{Ge}}\cdot$

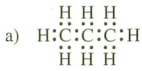
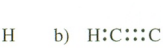
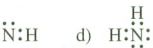
1.2 a) $\cdot Ca\cdot + 2\ :\ddot{\underset{\cdot\cdot}{Cl}}\cdot \longrightarrow Ca^{2+} + 2\ :\ddot{\underset{\cdot\cdot}{Cl}}:^{-}$

b) $2\ Na\cdot + \cdot\ddot{\underset{\cdot\cdot}{S}}\cdot \longrightarrow 2\ Na^{+} + :\ddot{\underset{\cdot\cdot}{S}}:^{2-}$

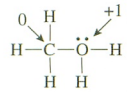
1.3 a) b) 

1.4

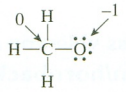
1.5 a) Stable, octet rule satisfied b) Unstable, 10 electrons on N

1.6 a)  b)  c) d) 

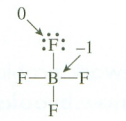
1.7

1.8 a) 

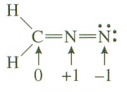
Total Charge = TC = +1

b) 

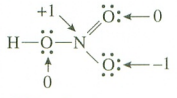
TC = –1

c) 

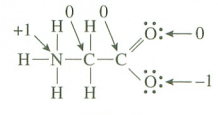
TC = –1

d) 

TC = 0

e) 

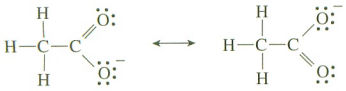
TC = 0

g) 

TC = 0

1.9 H—O—Cl more stable because of less formal charges

1.10

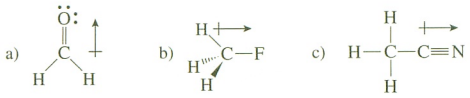


1.11 a) C—N b) O—N c) O—Cl d) C—Cl e) B—O f) C—Mg g) Not polar h) Not polar

1.12 a) Linear b) Trigonal planar c) Tetrahedral

1.13 a) Tetrahedral at C, bent at O (tetrahedral) b) Trigonal planar at C, bent at N (trigonal planar)
c) Trigonal planar at C, bent at O (trigonal planar)

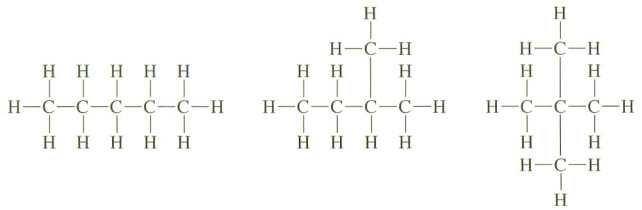
1.14



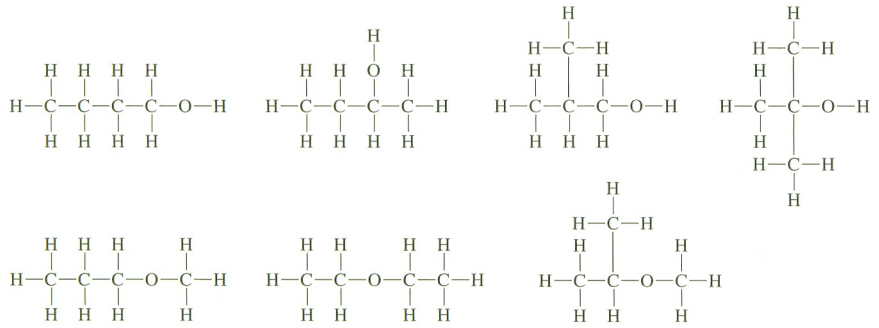
CHAPTER 2

2.1 a) Less stable, octet rule satisfied but charge on C b) Stable, octet rule satisfied c) Very unstable, octet rule not satisfied at N d) and e) Stable, octet rule satisifed

2.2



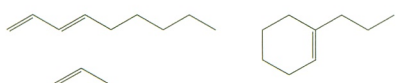
2.3



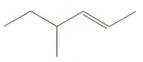
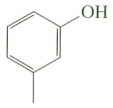
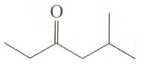
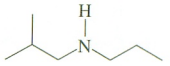
2.4 a) Same b) Same c) Isomers d) Same

2.5 a) DU = 0

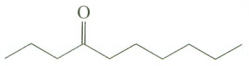
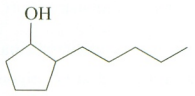
b) DU = 2

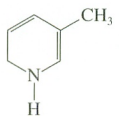
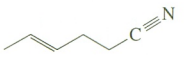


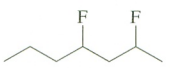
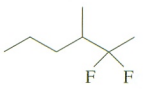
c) DU = 4

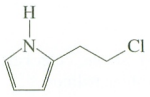
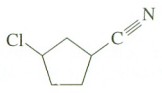
2.6 a)  b)  c)  d) 

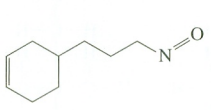
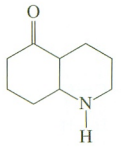
2.8 a) Same b) Same c) Isomers d) Same e) Same f) Isomers

2.9 a) DU = 1  

b) DU = 3  

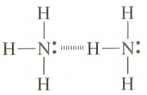
c) DU = 0  

d) DU = 3  

e) DU = 3  

2.10 a) 5 b) 4 c) 3 d) 7 e) 6

2.11 a) London b) Van der Waals c) Ion–ion d) Van der Waals and hydrogen bonding

2.12 

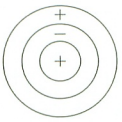
2.13 KBr because it is ionic

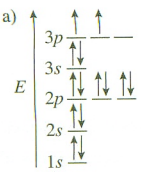
2.14 $CH_3CH_2CH_2OH$ because it can hydrogen bond

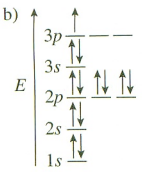
2.15 $CH_3CH_2CH_2CH_2CO_2H$ because it has a smaller nonpolar part

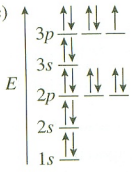
2.16 a) Ether b) Alcohol c) Carboxylic acid d) Amide e) Ester f) Arene and aldehyde

CHAPTER 3

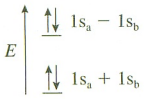
3.1 

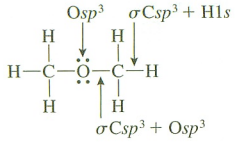
3.2 a) 

b) 

c) 

3.3 a) Excited state b) Excited state

3.4 

3.5 

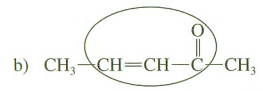
3.6 1) $\sigma Csp^2 + H1s$ 2) $\sigma Csp^3 + H1s$ 3) $\sigma Csp^3 + Csp^2$
4) $\sigma Csp^2 + Nsp^2$, $\pi C2p + N2p$ 5) $\sigma Csp^3 + Nsp^2$ 6) $\sigma Csp^3 + H1s$

3.7 a) *sp* at both
b) one sigma and two pi bonds
c) nonbonding *sp* AO on N

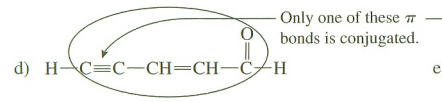
3.8 1) $\sigma Csp^2 + H1s$ 2) $\sigma Csp^3 + H1s$ 3) $\sigma Csp^3 + Csp^2$
4) $\sigma Csp^2 + Csp^2$, $\pi C2p + C2p$ 5) $\sigma Csp^2 + Csp$
6) $\sigma Csp + Csp$, 2 $\pi C2p + C2p$ 7) $\sigma Csp + H1s$

3.9 a) 1) $\sigma Csp^3 + H1s$ 2) $\sigma Csp^3 + Csp^2$ 3) $\sigma Csp^2 + H1s$ 4) $\sigma Csp^2 + Osp^2$, $\pi C2p + O2p$
b) 1) $\sigma Csp^3 + Csp^2$ 2) $\sigma Csp^2 + Csp^2$, $\pi C2p + C2p$ 3) $\sigma Csp^2 + Csp$
4) $\sigma Csp + Nsp$, 2 $\pi C2p + N2p$ 5) $\sigma Csp^2 + H1s$
c) 1) $\sigma Csp^2 + Osp^2$, $\pi C2p + O2p$ 2) $\sigma Csp + H1s$ 3) $\sigma Csp + Csp$, 2 $\pi C2p + C2p$
4) $\sigma Csp^2 + Csp$ 5) $\sigma Csp^3 + Csp^2$ 6) $\sigma Csp^3 + H1s$
d) 1) $\sigma Csp^3 + H1s$ 2) $\sigma Csp^3 + Csp^3$ 3) $\sigma Csp^3 + Nsp^3$ 4) $\sigma Nsp^3 + H1s$

3.10 a) None

b) 

c)

d) 

e) None

3.11 a) 1) sp^3 2) sp^2 3) sp^2 4) sp^2 5) sp^3
b) 1) sp^3 2) sp^2 3) sp^2 4) sp^3
c) 1) sp^2 2) sp^2 3) sp^2 4) sp^3
d) 1) sp^2 2) sp^2

3.12 a) These are not resonance structures because atoms have moved.
b) These are resonance structures.
c) These are not resonance structures because atoms have moved.

3.13 a) Two electrons are missing from the structure on the right.

b) The structure on the right has 5 bonds to C and 2 more electrons.

c) In the structure on the right, the center N has only 6 electrons.

d) The C bonded to O has 5 bonds (10 electrons) in the right structure.

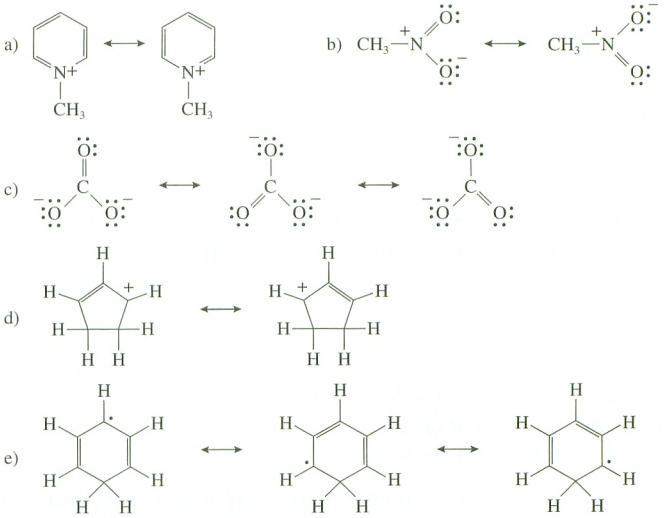
3.14 a) The right structure is less important because it has formal charges and the octet rule is not satisfied at one C.

b) The first two structures are equally important; the last structure is less important because it has more formal charges and the octet rule is not satisfied at the N.

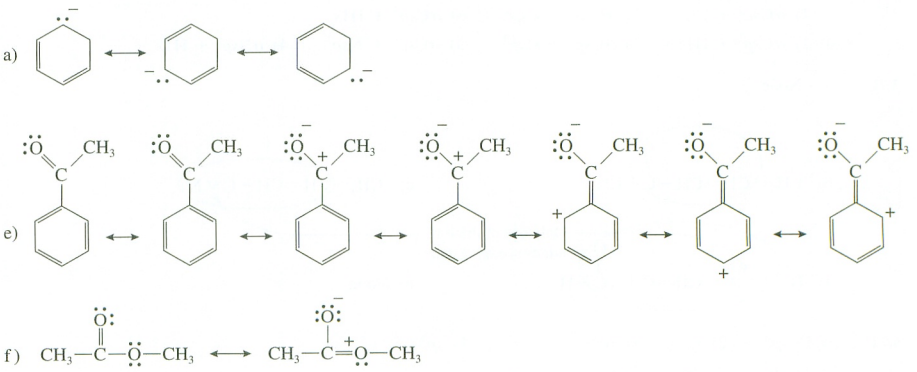
3.15 a) The second structure makes only a minor contribution because it does not satisfy the octet rule. The compound has only a small (but important) amount of resonance stabilization.

b) The first two structures, plus one additional similar structure, contribute equally; the last structure can be neglected. The ion has a large amount of resonance stabilization.

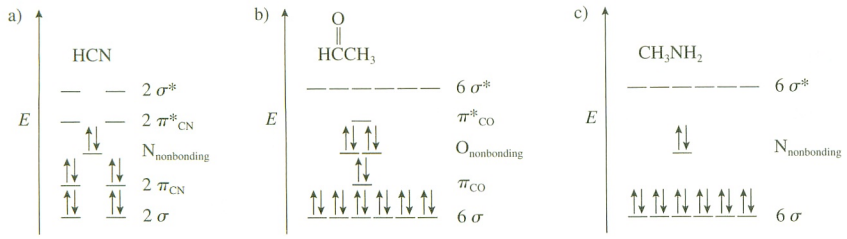
3.16



3.17



3.18



CHAPTER 4

4.1 a) Acid b) Both c) Acid d) Base e) Both f) Both g) Both

4.2 a) $CH_3-\overset{+}{\underset{\displaystyle H}{\underset{|}{O}}}-H$ b) $H-\ddot{O}-H$ c) $CH_3-\overset{+}{N}H_3$

4.3 a) $H-\ddot{O}:^-$ b) $H-\ddot{O}:$ (H) c) $H-\ddot{N}:^-$ (H) d) $H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}:^-$

4.4 a) $:\ddot{N}H_2^- + H-\ddot{O}-H \rightleftharpoons :NH_3 + :\ddot{O}-H^-$ (Base, Acid, Conjugate acid, Conjugate base)

b) $CH_3\ddot{O}:^- + H-\overset{H}{\overset{+}{O}}-H \rightleftharpoons CH_3\ddot{O}-H + H-\ddot{O}-H$

4.5 a) Lewis acid b) Lewis base c) Lewis acid d) Lewis base e) Both

4.6 a) $K_a = 1 \times 10^4$ b) $pK_a = 16$ c) $K_a = 1 \times 10^{-38}$ d) $pK_a = -6$

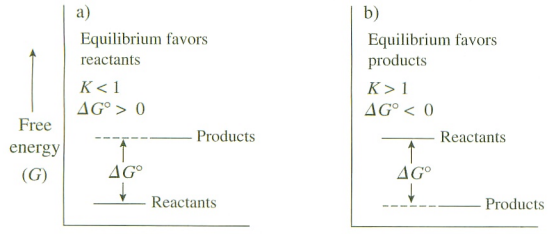
4.7 a) Stronger b) Weaker c) Stronger d) Weaker

4.8 a) Stronger b) Stronger c) Weaker d) Weaker

4.9 a) Favors reactants b) Favors products

4.10 a) Favors products b) Favors products

4.11



4.13 a) HCl b) PH_4^+ c) H_2S

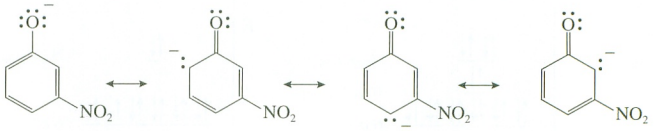
4.14 a) HO^- b) CH_3NH^-

4.15 a) $H_2NCH_2CH_2O-\textcircled{H}$ b) $CH_3CH_2O-\textcircled{H}$ c) $CH_3S-\textcircled{H}$

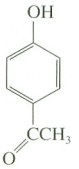
4.16 a) CHF_2CO_2H b) CHF_2CO_2H c) $CH_3OCH_2CO_2H$

4.17 $CH_3CH_2C{\equiv}C-\textcircled{H}$

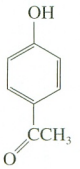
4.18



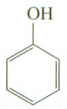
4.19 a) $CH_3\overset{O}{\overset{\|}{C}}CH_2C{\equiv}N$ b)



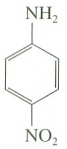
c)



d) $CH_3\overset{O}{\overset{\|}{C}}OCH_3$ e)



4.20 a)



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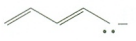


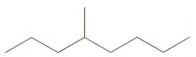
4.21 a) Products b) Products c) Reactants

4.22 Answers a) and c) are acceptable because they have no H acidic enough to protonate the anion; b) is not acceptable because the H on the O is too acidic.

CHAPTER 5

5.1 a) 2-Methylpentane b) 2-Methylpentane c) 2,4-Dimethylhexane
d) 5-Ethyl-3-methyl-5-propylnonane e) 3-Ethyl-2,5-dimethylhexane f) 3-Ethyl-2,6-dimethylheptane

5.2 a)



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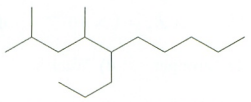
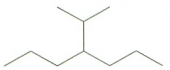


5.3 a) 4-Ethyl-2,2-dimethylhexane b) 2,2-Dimethylpentane

5.4 a) (2-Methylpentyl) b) (1-Methylpropyl) c) (2,2-Dimethylpropyl)

5.5 a) 4-(1-Methylethyl)heptane b) 5-(1,2-Dimethylpropyl)decane

5.6 a)



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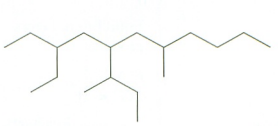
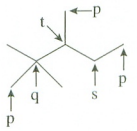


5.7 a)



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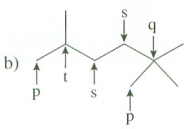
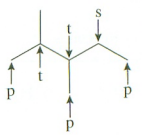
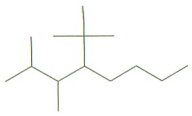


c)



5.8 4-Isopropylheptane

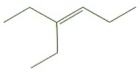
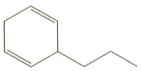
5.9



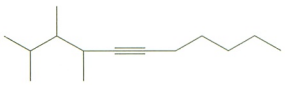
5.10 a) 1,2-Dimethylcyclopentane b) (1-Methylpropyl)cyclohexane
c) 5-Cyclopentyl-2-methylheptane d) 1-Ethyl-3,5-dimethylcyclooctane

5.11 a) b)

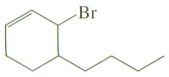
5.12 a) 2,4-Dimethyl-2-hexene b) 2-Methyl-1,3,5-cycloheptatriene c) 3-Ethyl-1,2-dimethylcyclopentene

5.13 a)  b) c) 

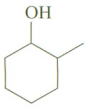
5.14 a) 3-Isopropyl-1-heptyne b) 2-Methylpent-1-en-3-yne c) 3-(2-Methylpropyl)-1,4-hexadiyne

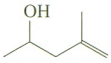
5.15 a) $HC{\equiv}CCH_2CH_2CH_3$ b) 

5.16 a) 5-Bromo-2,4,4-trimethylheptane b) 1-Chloro-3-ethyl-1-methylcyclopentane

5.17 

5.18 a) 2-Butanol b) 3-Methyl-3-hexanol c) 3-Cyclopentyl-1-propanol
d) 3-Bromo-3-methylcyclohexanol

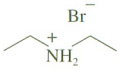
5.19 a) 

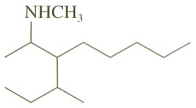
b) 

5.20 a) Ethyl methyl ether b) 1-Chloro-3-methoxycyclopentane

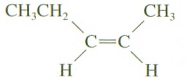
5.21 a) Propylamine b) *N*-Ethylcyclopentylamine

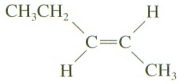
5.22 a) *N*,5-Dimethyl-2-hexanamine b) 5-Amino-2-hexanol

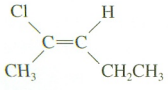
5.23 a) 

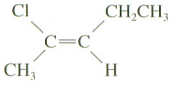
b) 

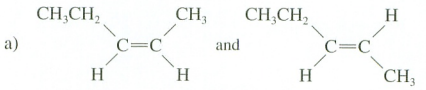
CHAPTER 6

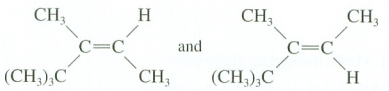
6.1 a) 

and 

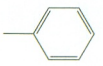
b) None
c) None d) 

and 

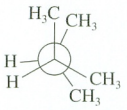
6.2 a)  and

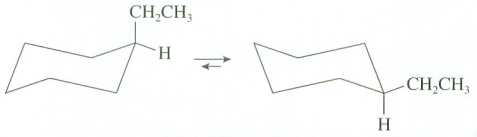
b) 

In both cases the right isomer is more stable because the larger groups are trans.

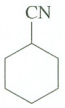
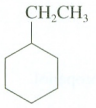
6.3 a) $-CH_2CH_3$ b) $-C(=O)OH$ c) $-CH_2CH_2CH_2CH_3$ d) $-C\equiv N$ e) 

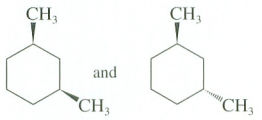
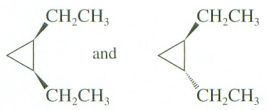
6.4 a) *E* b) *E* c) *Z*

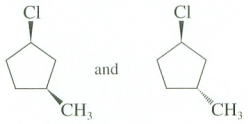
6.6 

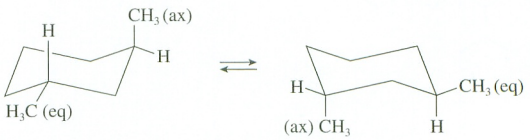
6.7 

The conformation on the right, with the ethyl group equatorial, is more stable.

6.8 a)  b)  c)

6.10 a)  b) 

c) 

6.11 

6.12 a) One methyl is axial, and one is equatorial.

b) Both methyls are axial in one conformation, and both are equatorial in the other.

c) The *trans*-isomer is more stable because it has a conformation with both methyls equatorial.

6.13 a) The conformation with both groups equatorial is the more stable conformation of the *cis*-stereoisomer. The conformation with the isopropyl group equatorial and the hydroxy group axial is the more stable conformation of the *trans*-stereoisomer.

b) The *cis*-stereoisomer is more stable than the *trans*-stereoisomer by 0.9 kcal/mol (3.8 kJ/mol).

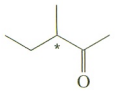
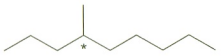
6.14 a) The methyls are trans; the *t*-Bu is cis to the closer methyl; all are equatorial; the conformation shown is more stable; the stereoisomer shown is most stable.

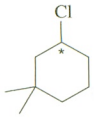
b) The chlorines are trans; both are axial; the ring-flipped conformation is more stable; the stereoisomer shown is more stable.

c) The groups are trans; the methyl is axial; the phenyl is equatorial; the conformation shown is more stable; the *cis*-stereoisomer is more stable.

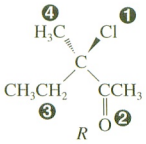
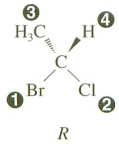
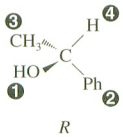
CHAPTER 7

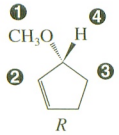
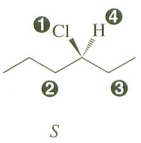
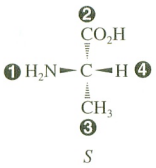
7.1 a) Achiral b) Chiral c) Chiral d) Achiral e) Chiral f) Chiral

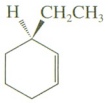
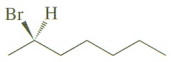
7.2 a) Not b) Not c)  d) 

e)  f) Not

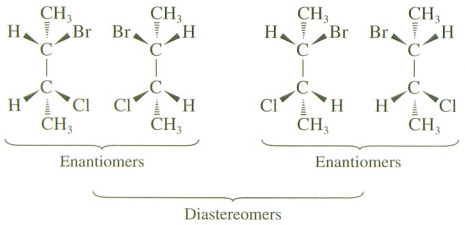
7.3 a) Yes b) Yes c) No d) Yes e) No f) Yes g) Yes h) No

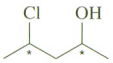
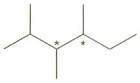
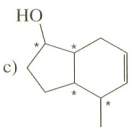
7.4 a)  b)  c) 

d)  e)  f) 

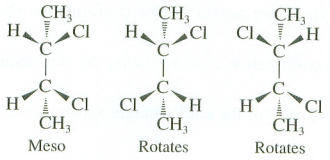
7.5 a)  b) 

7.6 a) False b) False c) True d) Cannot be determined e) True

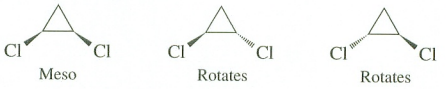
7.7 

7.8 a)  4 b)  4 c)  16 d) None

7.9

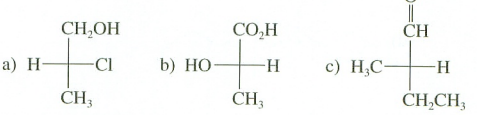


7.10



7.11 a) Yes b) No, meso c) Yes d) No, meso

7.12

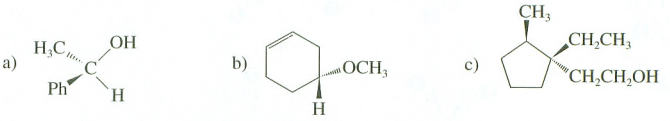


7.13 a) *S* b) *S*

7.14 a) Chiral b) Chiral c) Not chiral d) Chiral e) Not chiral f) Chiral

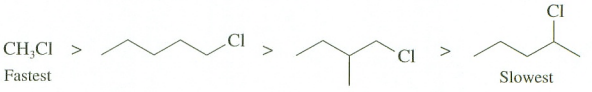
CHAPTER 8

8.1



8.2 a) The right compound reacts faster because it has less steric hindrance.
b) The right compound reacts faster because it has less steric hindrance.
c) The left compound reacts faster because of resonance stabilization of the transition state.

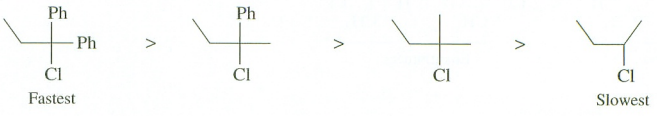
8.3



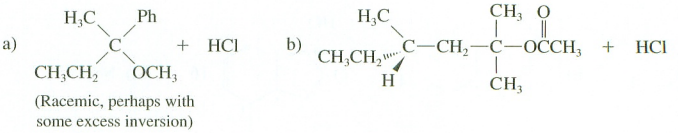
8.5 Approximately half broken

8.6 a) Left; tertiary carbocation is more stable
b) Left; resonance stabilized carbocation is more stable
c) Left; resonance stabilized carbocation is more stable
d) Right; methoxy group provides extra resonance stabilization of the carbocation

8.7



8.8



8.9 a) Primary substrates with a strong nucleophile (hydroxide ion) react by the S_N2 mechanism. The right reaction is faster because mesylate ion is a better leaving group than chloride ion.

b) Tertiary substrates react by the S_N1 mechanism. The right reaction is faster because iodide ion is a better leaving group than bromide ion.

8.11 a) Because the leaving group is on a tertiary carbon, the reaction proceeds by an S_N1 mechanism. The reactivity of the nucleophile does not affect the rate of an S_N1 reaction, so both reactions proceed at the same rate.

b) Because the leaving group is on a primary carbon, the reaction proceeds by an S_N2 mechanism. The right reaction is faster because the nucleophile is stronger. (Nucleophile strength increases down a column of the periodic table.)

c) Because the leaving group is on a primary carbon, the reaction proceeds by an S_N2 mechanism. The left reaction is faster because the nucleophile is stronger. (It is a stronger base.)

8.12 a) S_N2 $CH_3CH_2\underset{\displaystyle :\ddot{Cl}:}{\underset{|}{C}}HCH_3 + {}^{-}\!:\ddot{S}H \longrightarrow CH_3CH_2\underset{\displaystyle :\ddot{S}H}{\underset{|}{C}}HCH_3 + :\ddot{Cl}:^{-}$

b) S_N1 $CH_3CH_2\overset{\displaystyle CH_3}{\overset{|}{C}}CH_3 \longrightarrow CH_3CH_2\overset{\displaystyle CH_3}{\overset{|}{C}}CH_3 + :\ddot{Br}:^{-}$

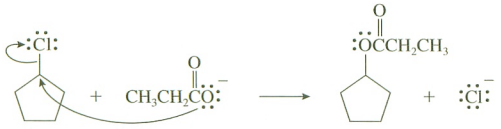
$CH_3CH_2\ddot{O}H$

$CH_3CH_2\overset{\displaystyle CH_3}{\overset{|}{C}}CH_3$ $\quad$ $CH_3CH_2\overset{\displaystyle CH_3}{\overset{|}{C}}CH_3$

$:\ddot{O}-CH_2CH_3 \longleftarrow$ $\quad$ $H-\overset{+}{\ddot{O}}-CH_2CH_3$

$+ \; H-\ddot{Br}:$ $\quad$ $:\ddot{Br}:^{-}$

c) S_N2 $CH_3CH_2CH_2CH_2\underset{\displaystyle :\ddot{O}Ts}{\underset{|}{C}}H_2 + \ddot{N}H_2CH_3 \longrightarrow CH_3CH_2CH_2CH_2\underset{\displaystyle TsO:^{-}}{\underset{|}{C}}H_2 + \overset{+}{N}H_2CH_3$

d) S_N2 

8.15 a) This S_N1 reaction is faster in the more polar solvent, methanol.

b) This S_N2 reaction, with a negative nucleophile, is faster in the less polar solvent, pure methanol.

c) This S_N2 reaction is faster in the aprotic solvent, DMSO.

8.16 a) Tertiary, so S_N1

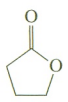
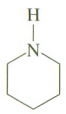
b) Secondary, with a strong nucleophile and an aprotic solvent, so S_N2

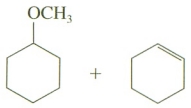
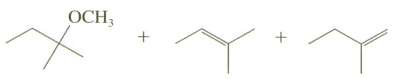
c) Methyl substrate (less hindered than primary), so S_N2

d) Allylic substrate, weak nucleophile and polar solvent, so S_N1

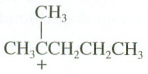
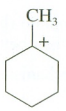
e) Allylic substrate, strong nucleophile and aprotic solvent, so S_N2

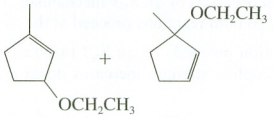
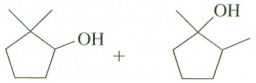
f) Secondary benzylic substrate, weak nucleophile and polar solvent, so S_N1

8.17 a)  b) 

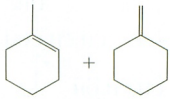
8.18 a)  b) 

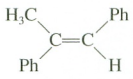
c)

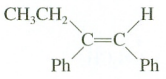
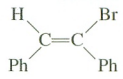
8.19 a) b)  c) 

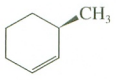
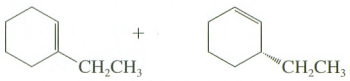
8.20 a)  b) 

CHAPTER 9

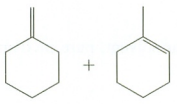
9.1 a) $CH_3CH{=}CHCH_2CH_3$ b) c) 

9.2 

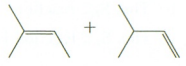
9.3 a)  b) 

9.5 a)  b) 

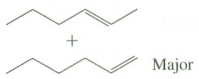
9.6 The bulky *t*-Bu group must be equatorial in both cases. The isomer on the left has the OTs group axial, so it can readily undergo E2 elimination. The isomer on the right has the OTs group equatorial, so it cannot readily react.

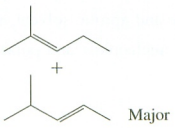
9.7 a) 
Major

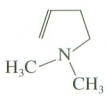
b)
cis + trans
Major

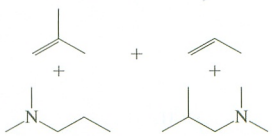
c) 
Major

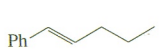
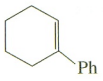
9.8 (*E*)-2-Butene is the major product because it is more stable and the conformation leading to it is more stable.

9.9 a) 
Major

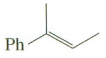
b) 
Major

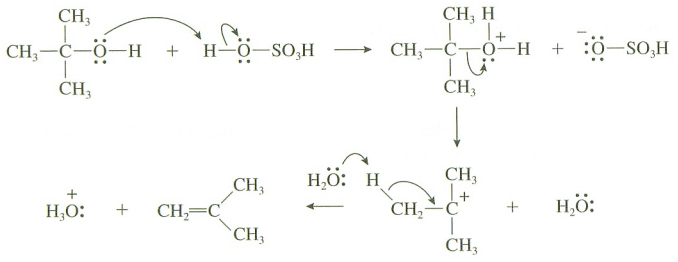
c) 

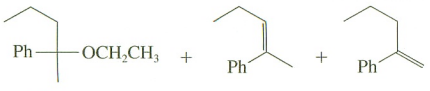
d) 
Major

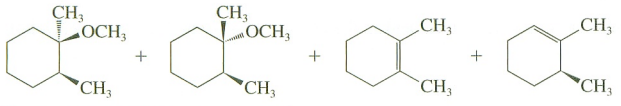
9.10 a)  b) 

c)
Major

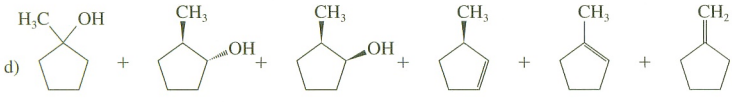
d) 

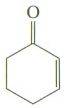
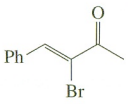
9.11 

9.13 a) 
Major

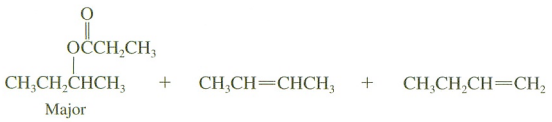
b) 
Major

c) Same as (b)

d) 
+ Ethyl ethers corresponding to the alcohols

9.14 a)  b) 

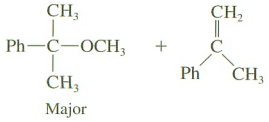
9.15 a) A secondary substrate with a weak base reacts predominately by the S_N2 mechanism. Minor amounts of E2 products may also be formed.


Major

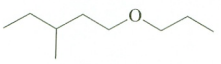
b) A secondary substrate with a strong base reacts predominately by the E2 mechanism.

Major

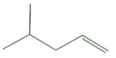
c) A tertiary substrate in the absence of a strong base reacts by the S_N1 and E1 mechanisms.


Major

9.16 a) The leaving group is on a primary carbon, so an S_N2 reaction occurs.

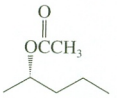


b) A primary substrate with a very hindered base gives predominately E2 elimination.

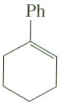


c) A secondary substrate with a strong base gives predominately E2 elimination.

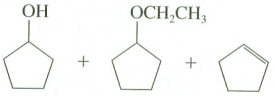
d) A secondary substrate with a weak base that is moderately nucleophilic in an aprotic solvent favors an S_N2 reaction. The reaction occurs with inversion of configuration.



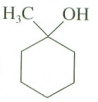
e) A tertiary substrate with a strong base favors E2 elimination.



f) A secondary substrate in a polar solvent and in the absence of a strong base or nucleophile favors the S_N1 and E1 reactions.

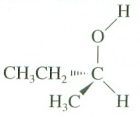


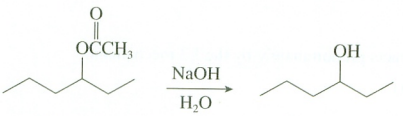
CHAPTER 10

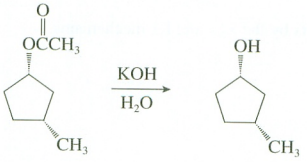
10.1 a) $CH_3CH_2CH_2CH_2OH$ b)  c) $CH_2{=}CHCH_2OH$

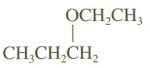
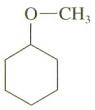
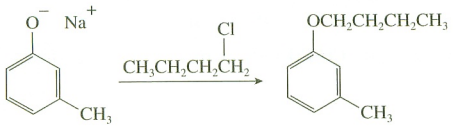
10.2 This is an S_N1 reaction, so only the chlorine bonded to the tertiary carbon is replaced.

10.3 Stereochemistry is retained because the CO bond of the product is not broken in the reaction.



10.4 a) 

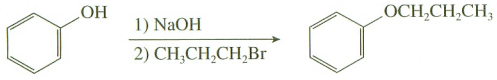
b) 

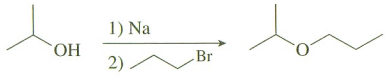
10.5 a)  b)  c) 

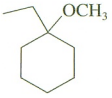
10.7 a) The right route is better because the left route gives primarily E2 elimination.

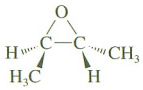
b) The right route is better because elimination cannot occur.

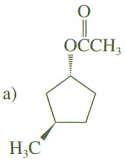
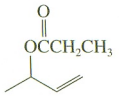
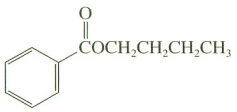
10.8 a) $CH_3CH_2CH_2CH_2OH \xrightarrow[2)\ CH_3I]{1)\ Na} CH_3CH_2CH_2CH_2OCH_3 \xleftarrow[2)\ CH_3CH_2CH_2CH_2Br]{1)\ Na} CH_3OH$

b) 

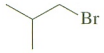
c) 

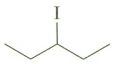
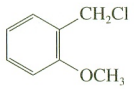
10.9 a)  b) $CH_3COCH_2CH_3$ (with CH_3 on C) c) $Ph_2CHOCH_2CH_2Cl$

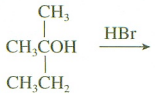
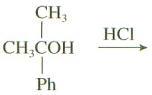
10.12 

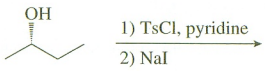
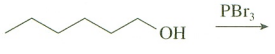
10.14 a)  b)  c) 

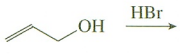
10.16 a) b) c) d) $CH_3CH_2CH_2I$

e) f) g) 

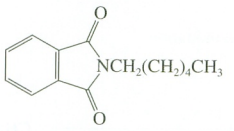
h)  i) j) 

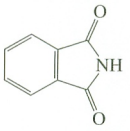
10.17 a)  b) 

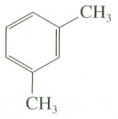
c)  d) 

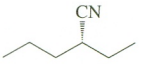
e)  f) $CH_3CH_2CH_2CH_2OH \xrightarrow{SOCl_2}$

10.18 a) $(CH_3CH_2)_2\overset{+}{N}(H)CH_2CH_3\ Br^-$ b) $CH_3CH_2\overset{+}{N}(CH_3)_2CH_3\ I^-$

10.19 a)  $\xrightarrow[H_2O]{NaOH}$ $CH_3(CH_2)_4CH_2NH_2$

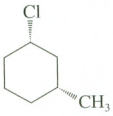
10.20  $\xrightarrow[3)\ NaOH,\ H_2O]{1)\ KOH;\ 2)\ PhCH_2CH_2Br}$ $PhCH_2CH_2NH_2$

10.21 a) b) 

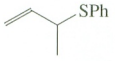
10.22 a) $PhCH_2CN$ b) $CH_3C{\equiv}C{-}CH_2CH_2CH_3$ c) 

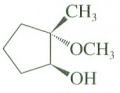
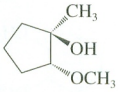
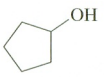
d) $HC{\equiv}CCH_2CH_3 \xrightarrow[2)\ CH_3I]{1)\ NaNH_2} CH_3C{\equiv}CCH_2CH_3$

e) f) + $HC{\equiv}CH$

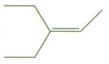
10.23 a)  $\xrightarrow[DMSO]{NaCN}$ b) $BrCH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_3 \xrightarrow[NH_3(l)]{HC{\equiv}C:^-\ Na^+}$

c) $CH_3C{\equiv}CH \xrightarrow[2)\ PhCH_2Br]{1)\ NaNH_2}$

10.24 a)  b) $Ph_3\overset{+}{P}{-}CH_2CH_2CH_3\ Br^-$ c) $CH_3CH_2CH_2CH_2SCH_3$ d)

10.25 a)  b)  c) 

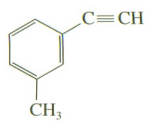
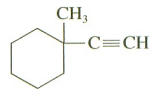
10.26 a) $CH_3CH_2CH{=}CH_2$ b) c) +

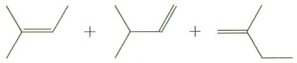
Major Minor d) 

10.27 a) No. The alkene shown would be a minor product according to Zaitsev's rule.

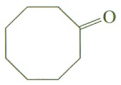
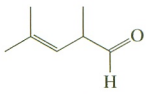
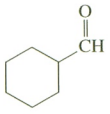
b) Yes. The alkene shown would be the major product because it is conjugated.

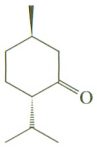
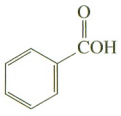
10.28 The top reaction is better because it can produce only the desired alkene. The bottom reaction would produce 1-pentene also.

10.29 a)  b) 

10.30 a) b) c) 

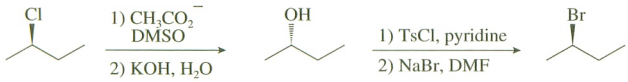
Major Minor Minor

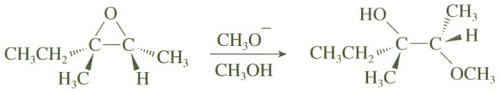
10.31 a)  b)  c) 

d)  e) 

10.32 a) $CH_3CH_2CH_2CH_2Br \xrightarrow[2)\ KOH,\ H_2O]{1)\ \text{phthalimide-K}^+} CH_3CH_2CH_2CH_2NH_2 \xrightarrow{\text{excess } CH_3I} CH_3CH_2CH_2CH_2\overset{+}{N}(CH_3)_3\ I^-$

b) $CH_3CH_2CHBr \xrightarrow[2)\ KOH,\ H_2O]{1)\ CH_3CO_2^-,\ DMSO} CH_3CH_2CHOH \xrightarrow[2)\ CH_3CH_2I]{1)\ Na} CH_3CH_2{-}O{-}CHCH_2CH_3$

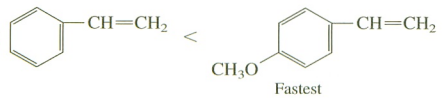
c) 

d) 

e) $HC{\equiv}CH \xrightarrow[2)\ PhCH_2Cl]{1)\ NaNH_2} PhCH_2C{\equiv}CH \xrightarrow[2)\ CH_3I]{1)\ NaNH_2} PhCH_2C{\equiv}CCH_3$

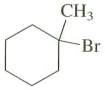
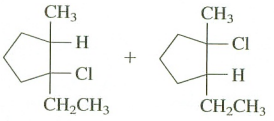
CHAPTER 11

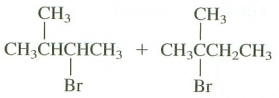
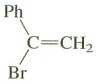
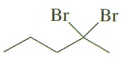
11.1 a) $\underset{\text{Slowest}}{CH_2{=}CH_2} < CH_3CH_2CH{=}CH_2 < \underset{\text{Fastest}}{CH_3CH_2\overset{CH_3}{\overset{|}{C}}{=}CH_2}$

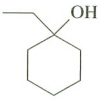
b) $CH_3CH{=}CH_2 <$  $<$

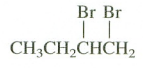
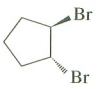
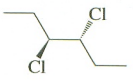
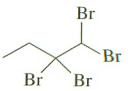
Slowest Fastest

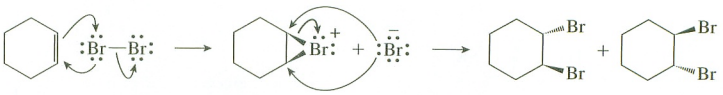
11.3 a) b) c)

d)  e) 

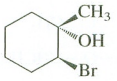
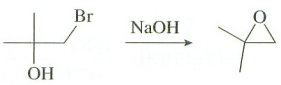
11.4 a)  b)  c) 

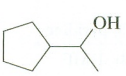
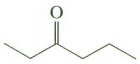
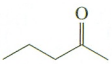
11.5 a) b)  c)

11.7 a)  b)  c)  d) 

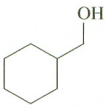
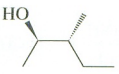
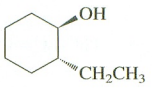
11.8 

11.9 The right one reacts faster because the methyl group makes the double bond more nucleophilic.

11.10 a)  b) 

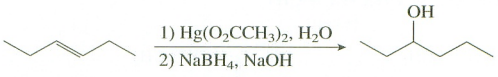
11.13 a) b)  c)  d) 

11.14 The left synthesis is better because only 3-hexanone, the desired ketone, is produced. The right reaction also produces 2-hexanone.

11.15 a)  b)  c) 

11.16

The alcohol on the right is the major product because the boron prefers to bond to the less hindered carbon of the alkene.

11.17 a) 

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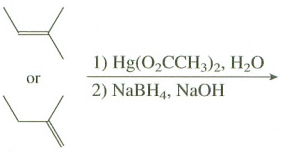
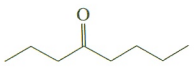
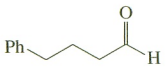
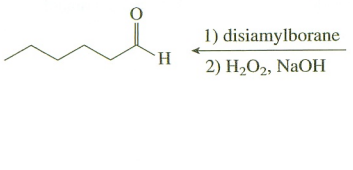
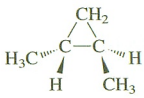
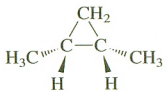
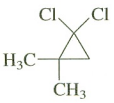
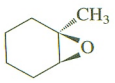
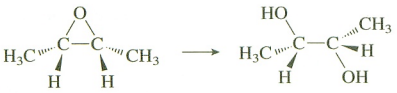
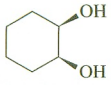
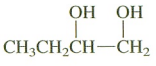
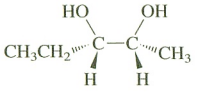
c) 

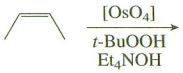
11.18 a)  b) 

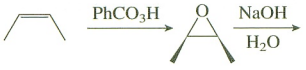
11.19 b) 

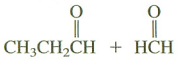
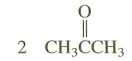
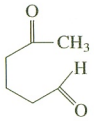
11.22 a)  b)  c) d) 

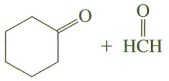
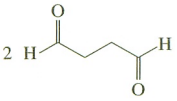
11.23 a)  b) 

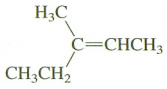
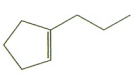
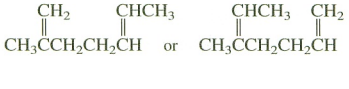
11.24 a)  b)  c) 

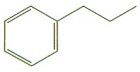
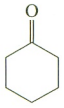
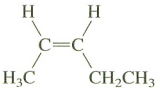
11.25 a) 

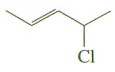
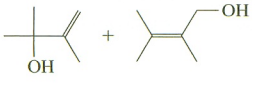
b) 

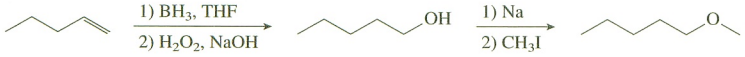
11.26 a)  b)  c) 

d)  e) 

11.27 a)  b)  c) 

11.28 a)  b)  c) $CH_3CH_2CH_2CH_2CH_3$ d)  e)

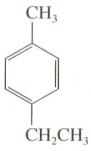
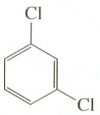
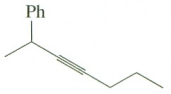
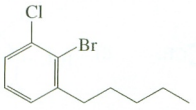
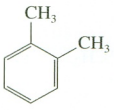
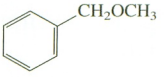
11.30 a)  b) 

11.31 a) 

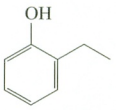
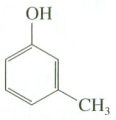
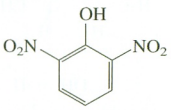
b)

CHAPTER 12

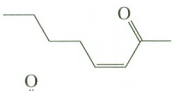
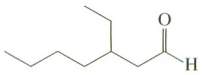
12.1 a) (1-Methylpropyl)benzene b) *o*-Chlorotoluene c) 1-Bromo-4-methoxybenzene
d) 4-Butyl-3-chlorotoluene e) 3-Ethyl-4-phenylcyclohexene f) 3-Phenyl-1-butanol

12.2 a) 
b) 
c) 
d) 
e) 
f) 

12.3 a) *m*-Propylphenol b) 3,5-Dibromophenol c) *p*-Methoxyphenol

12.4 a) 
b) 
c) 

12.7 a) Hexanal b) 5-Methyl-3-hexanone c) (*Z*)-4-Methyl-2-hexenal d) *p*-Chlorobenzaldehyde
e) 5-(2-Methylpropyl)-3-cycloheptenone f) 2,4-Pentanedione g) 3-Phenylcyclopentanone
h) 4-Methylpent-3-en-2-one

12.8 a) 
b) 
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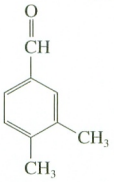
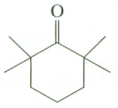
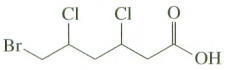
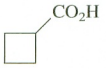
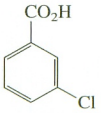
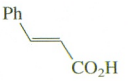
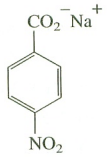
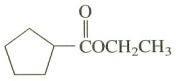
d) 
e)
f) 

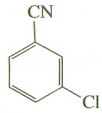
12.11 a) 3-Methylpentanoic acid b) *p*-Bromobenzoic acid c) (*Z*)-4,4-Dichloro-2-pentenoic acid
d) 2-Cyclohexenecarboxylic acid e) 3-Methyl-4-nitrobenzoic acid f) 3-Cyclopropylbutanoic acid

12.12 a) 
b) 
c) 
d) 

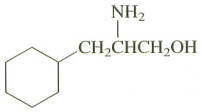
12.14 a) Benzoyl chloride b) Propanoic anhydride c) Methyl propanoate
d) Propyl 3-ethylbenzoate e) Cyclopentyl 4-methylpentanoate f) *N*-Methyl-3-pentynamide
g) Isopropyl 3-cyanocyclopentanecarboxylate h) Pentanenitrile i) Potassium 2-methylpentanoate

12.15 a) $CH_3CH_2\overset{O}{\overset{\|}{C}}Cl$ b) $CH_3\overset{O}{\overset{\|}{C}}N(CH_3)_2$ c) $CH_3(CH_2)_3\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}(CH_2)_3CH_3$ d) 

e) $CH_3(CH_2)_4\overset{O}{\overset{\|}{C}}NH_2$ f) $CH_3\overset{O}{\overset{\|}{C}}\overset{CH_3}{\overset{|}{C}}HCH_3$ g) $Ph\overset{O}{\overset{\|}{C}}CH_2Ph$ h) 

i)  j) $CH_3CH_2CH_2CH_2\overset{CH_3}{\overset{|}{C}}HCH_2C{\equiv}N$

12.19 a) 4-Hydroxy-2-cyclohexenone b) 2-Amino-4-methylpentanoic acid
c) 1,4-Butanedioic acid d) Methyl 4-methyl-5-oxopentanoate
e) 3-Cyanobenzaldehyde f) 4-Ethyl-3-hydroxy-*N*-methylhexanamide
g) 3-Oxobutanenitrile h) Isopropyl 3-oxo-4-phenylhexanoate

12.20 a) $HO\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}OH$ b) $CH_3CH_2\overset{OH}{\overset{|}{C}}(CH_2CH_3)\overset{O}{\overset{\|}{C}}CH_2CH_3$ c) 

d) $CH_3CH_2CH{=}CHCH_2CH_2\overset{OH}{\overset{|}{C}}H\overset{O}{\overset{\|}{C}}\overset{CH_3}{\overset{|}{C}}OCH_3$ e) $CH_3\overset{CH_3}{\overset{|}{C}}H\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}N(CH_3)_2$ f) $Ph\overset{NH_2}{\overset{|}{C}}H\overset{O}{\overset{\|}{C}}OH$

CHAPTER 13

13.1 a) 3.33×10^{-3} cm b) 9.68×10^{14} s^{-1} c) 0.858 kcal/mol (3.59 kJ/mol)
d) 92.3 kcal/mol (387 kJ/mol)

13.2 Infrared

13.3 3.8×10^{-5} kcal/mol (1.6×10^{-4} kJ/mol)

13.4 a) C—H, lighter atom b) C≡C, stronger bond c) C—Cl, lighter atom and stronger bond

13.5 a) OH, 3000 cm^{-1}, very broad; =CH, 3100–3000 cm^{-1}; —CH, 3000–2850 cm^{-1}
b) =CH, 3100–3000 cm^{-1}; —CH, 3000–2850 cm^{-1}
c) NH_2, two bands, 3400–3250 cm^{-1}; =CH, 3100–3000 cm^{-1}
d) OH, 3550–3200 cm^{-1}, broad; =CH, 3100–3000 cm^{-1}; —CH, 3000–2850 cm^{-1}
e) NH, one band, 3400–3250 cm^{-1}; —CH, 3000–2850 cm^{-1}
f) —CH, 3000–2850 cm^{-1}; CHO, 2830–2700 cm^{-1}, two bands

13.6 The band in the triple bond region at 2150–2100 cm^{-1} is much stronger for 1-hexyne than it is for the more symmetrical 3-hexyne. In addition, the ≡CH band near 3300 cm^{-1} in the spectrum of 1-hexyne confirms the presence of the triple bond.

13.7 Most hydrocarbons have —CH bonds that absorb in the 3000–2850 cm^{-1} region.

13.8 a) 1745 cm^{-1} b) 1710–1690 cm^{-1} c) 1695–1675 cm^{-1}
d) 1720–1700 cm^{-1} e) 1690–1670 cm^{-1}

13.9 a) The left compound, a ketone, has its carbonyl absorption near 1715 cm^{-1}, whereas the right compound, an aldehyde, has its carbonyl peak near 1730 cm^{-1} and has two bands in the region of 2830–2700 cm^{-1}.
b) The left ester (nonconjugated) has its carbonyl absorption near 1740 cm^{-1}, whereas the right ester (conjugated) has its carbonyl absorption near 1720–1700 cm^{-1}.
c) The carboxylic acid has a very broad band near 3000 cm^{-1}.

13.10 a) 3100–3000, 3000–2850, 1695–1675, 1660–1640

b) 3400–3250 (two bands), 3100–3000, 3000–2850, 1600–1450 (four bands), 900–675

c) 3100–3000, 3000–2850, 1660–1640, 1300–1000

d) 3550–3200 (broad), 3000–2850, 1300–1000

e) 3300, 3000–2850, 2150–2100, 1550, 1380

f) 3100–3000, 3000–2850, 2830–2700 (two bands), 1710–1690, 1600–1450 (four bands), 900–675

13.11 a) 1-Butyne has absorptions at 3300 and 2150–2100 cm^{-1} that are not present in the spectrum of 1-butene.

b) Benzyl alcohol has absorptions at 3100–3000, 1600–1450, and 900–675 cm^{-1} that are not present in the spectrum of *t*-butanol.

c) Benzaldehyde has two bands at 2830–2700 cm^{-1} that are not present in the spectrum of the ketone, acetophenone.

d) The primary amine has two bands in the 3400–3250 cm^{-1} region, whereas the secondary amine has only one.

13.12 a) Ketone, no evidence for C=C

b) Carboxylic acid, no evidence for C=C

c) Conjugated aldehyde, has C=C, possibly aromatic ring

CHAPTER 14

14.1 a) 7.4 δ b) 1480 Hz on a 200-MHz and 2960 Hz on a 400-MHz instrument c) 7.4 δ

14.2 a) 3 b) 4 c) 5 d) 4 e) 2

14.3 a) $CH_3\overset{\overset{O}{\|}}{C}CH_2CH_3$ (2.2, >2.2, >0.9) b) $CH_3\overset{\overset{OH}{|}}{C}HCH_3$ (OH ← 2–5; >0.9, >3.3) c) $CH_3\overset{\overset{O}{\|}}{C}OCH_2CH_3$ (2.0, >3.7, >0.9) d) $CH_3\overset{\overset{Cl}{|}}{C}H\overset{\overset{Cl}{|}}{C}H_2$ (>0.9, >3.0; >3.0 (most downfield))

14.4 Triplet

14.6 a) $a = x = 3$ b) $a = 7, x = 2$ c) $a = 3, x = 2$ d) $a = 5, x = 2$ e) $a = 3, m = 6, x = 3$

14.7 a) CH_3CH_2OH

>0.9	>3.3	2–5
3	4	1
3	2	1

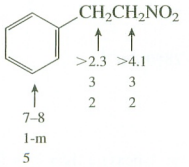
Chemical shift / number of lines / integral

b) $CH_3\overset{\overset{Cl}{|}}{C}HCH_3$

>0.9	>3.0
2	7
6	1

c) $CH_3CH_2OCH_2CH_3$

>0.9	>3.0
3	4
3	2

d) 

e) $CH_3\overset{\overset{O}{\|}}{C}OCH_2CH_3$

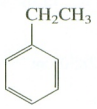
2.0	>3.7	>0.9
1	4	3
3	2	3

f) $CH_3CH_2CH_2Cl$

0.9	>0.9	>3.0
3	6-m	3
3	2	2

g) CH_3CHCl_2

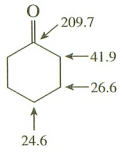
>0.9	>>3.0
2	4
3	1

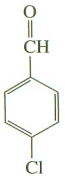
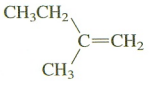
14.8 a) $CH_3\overset{\overset{O}{\|}}{C}CH_3$ b) 

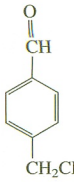
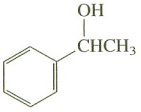
c) $CH_3\overset{\overset{O}{\|}}{C}H$

d) e) $CH_3\overset{\overset{O}{\|}}{C}O\overset{\overset{CH_3}{|}}{C}HCH_3$ f) $CH_3CH_2\overset{\overset{CH_3}{|}}{C}HCl$

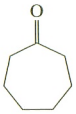
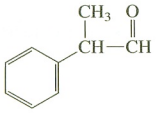
14.9 a) 1 b) 3 c) 6 d) 3

14.10 a) $CH_3CH_2CH_2CH_2OH$ (13.6, 19.1, 35.0, 61.4) b) 

14.11 a)  b)  c)

14.12 a)  b) $BrCH_2CH_2\overset{O}{\overset{\|}{C}}OCH_2CH_3$ c) 

14.13 $HOCH_2CH_2CH_2CH_2CH_2CH_2CH_2OH$

14.14 a) $CH_3CH_2\overset{CH_3}{\overset{|}{C}}HCH_2OH$ b)  c) 

CHAPTER 15

15.1 0.349

15.2 $2.0 \times 10^4\ M^{-1}\ cm^{-1}$

15.3 2.38×10^{-5} M

15.4 n $\longrightarrow \pi^*$

15.5 The absorption at 213 nm is due to a $\pi \longrightarrow \pi^*$ transition, and that at 320 nm is due to a n $\longrightarrow \pi^*$ transition.

15.6 a) The left ketone is conjugated and should absorb at longer wavelength than the right ketone, which is not conjugated.

b) The right compound is conjugated and should absorb at longer wavelength than the left compound, which is not conjugated.

c) The left compound has three conjugated double bonds and should absorb at longer wavelength than the right compound, which has only two conjugated double bonds.

d) Cyclohexanone has an absorption for a n $\longrightarrow \pi^*$ transition in the accessible UV region, whereas the alcohol shows no such absorption.

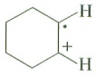
15.7 Butane = 58.0783; acetone = 58.0419

15.8 Butane = 4.4%; acetone = 3.3%

15.9 a) M : M + 2 : M + 4 = 1 : 0.67 : 0.11 (9:6:1)

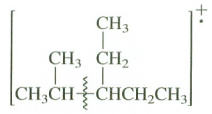
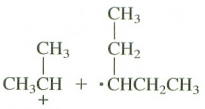
b) M : M + 2 : M + 4 = 1 : 1.33 : 0.33 (3:4:1)

15.10 a) Br is present. b) N is present.

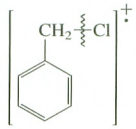
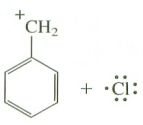
15.11 a) $CH_3\overset{+}{\dot{N}}HCH_3$ b) 

15.12 a) $[CH_3CH_2CH_2\!\!\sim\!\!CH_2CH_3]^{+\cdot} \longrightarrow CH_3CH_2\overset{+}{C}H_2 + \cdot CH_2CH_3$ (*m/z* 43)

$CH_3CH_2\dot{C}H_2 + \overset{+}{C}H_2CH_3$ (*m/z* 29)

15.13 a)  

(*m/z* 43)

15.14 a)  

(*m/z* 91)

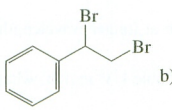
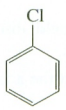
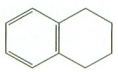
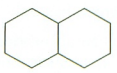
b) $CH_3CH_2CH_2\!\!\sim\!\!\overset{+}{\dot{O}}H \longrightarrow CH_3CH_2\dot{C}H_2 + \overset{+}{O}(H)=CH_2$ (*m/z* 31)

c) $CH_3CH_2\!\!\sim\!\!\overset{+}{O}\!\!=\!\!C\!\!\sim\!\!CH_2CH_2CH_2CH_3 \longrightarrow CH_3CH_2C\equiv\overset{+}{O}: + \dot{C}H_2CH_2CH_2CH_3$ (*m/z* 57)

$CH_3\dot{C}H_2 + :O\equiv\overset{+}{C}CH_2CH_2CH_2CH_3$ (*m/z* 85)

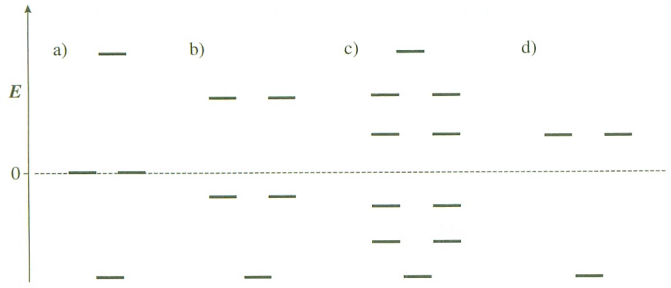
$CH_3CH_2C(=\overset{+}{O}H)=CH_2 + CH_2=CHCH_3$ (*m/z* 72 (McLafferty rearrangement))

CHAPTER 16

16.1 a)  b)  c)  d) 

16.2 (5) (28.6 kcal/mol) − 80 kcal/mol = 63 kcal/mol; yes
(5) (120 kJ/mol) − 335 kJ/mol = 265 kJ/mol; yes

16.3



16.7 a) 4 π electrons, so antiaromatic
b) 6 π electrons, so aromatic
c) 10 π electrons, so aromatic
d) 2 π electrons, so aromatic

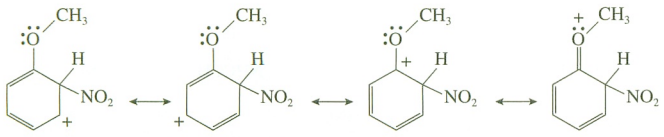
16.8 a) 6 π electrons, so aromatic
b) 6 π electrons, so aromatic
c) 6 π electrons, so aromatic
d) 6 π electrons, so aromatic
e) 6 π electrons, so aromatic
f) 8 π electrons, so antiaromatic if planar

16.12 a) Left compound because its conjugate base is aromatic
b) Right compound because conjugate base of left compound is antiaromatic
c) Right compound because its conjugate base is aromatic

16.13 Left compound because the carbocation that is formed from it is aromatic

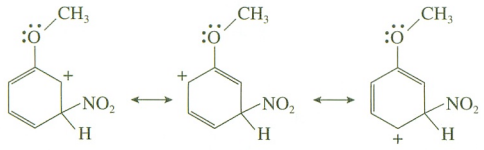
CHAPTER 17

17.1



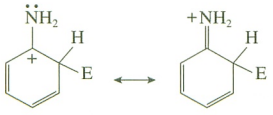
The last structure is especially stable because the octet rule is satisfied at all atoms.

17.2

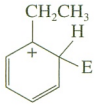


No especially stable resonance structure is formed.

17.3 a) The electron pair on the N can stabilize a positive charge on the adjacent carbon by resonance.

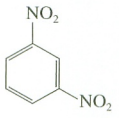
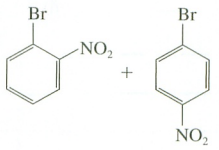


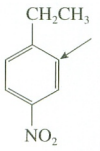
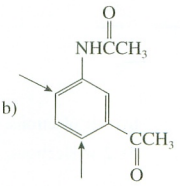
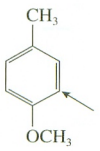
b) The ethyl group stabilizes a positive charge on the adjacent carbon by hyperconjugation.

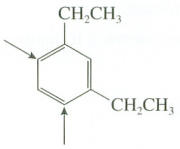
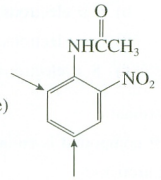
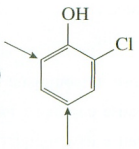


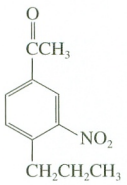
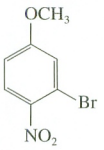
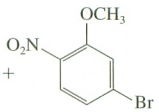
17.4 a) The electronegative fluorines make the CF_3 group electron withdrawing.
b) The positive nitrogen is an inductive electron-withdrawing group.

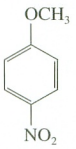
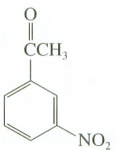
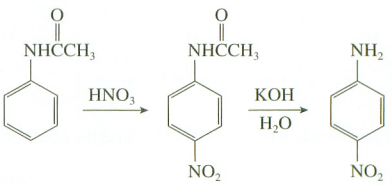
17.5 a) Activating, *o*/*p*-director b) Deactivating, *m*-director c) Deactivating, *m*-director

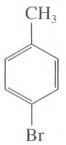
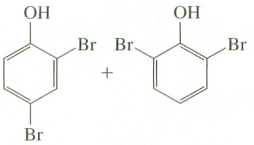
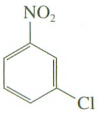
17.6 a)  b) 

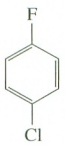
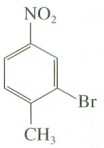
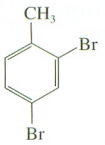
17.7 a)  b)  c) 

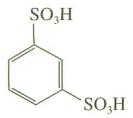
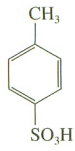
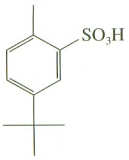
d)  e)  f) 

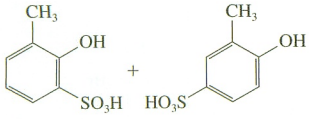
17.8 a)  b)  

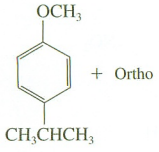
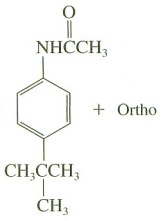
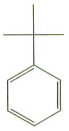
17.9 a)  + Ortho b)  c)  + Ortho + Ortho

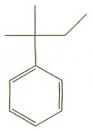
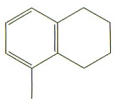
17.11 a)  + Ortho b)  c) 

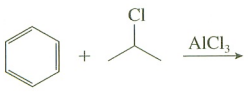
d)  + Ortho e)  f) 

17.13 a)  b)  + Ortho c) 

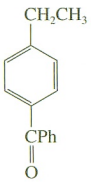
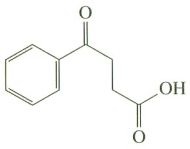
d) 

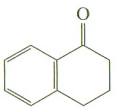
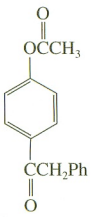
17.15 a)  + Ortho b)  + Ortho c) 

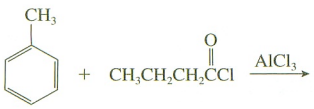
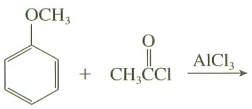
d)  e)  f) No reaction

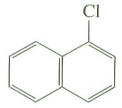
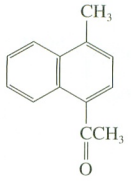
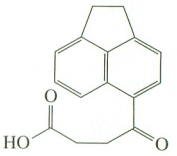
17.16 a) b) 

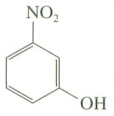
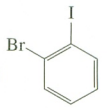
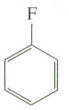
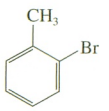
17.18 Both groups are weakly activating, but the position ortho to the methyl group is less sterically hindered than the position ortho to the isopropyl group.

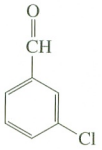
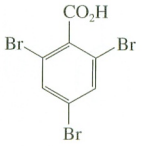
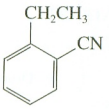
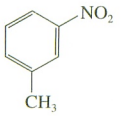
17.19 a)  b) No reaction c) 

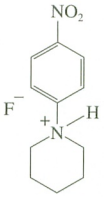
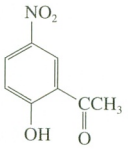
d)  e) 

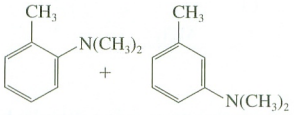
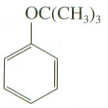
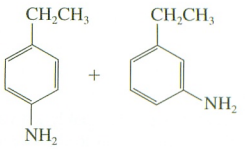
17.20 a)  b) 

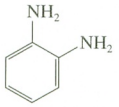
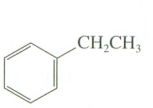
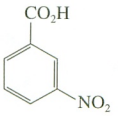
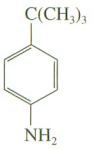
17.22 a)  b)  c) 

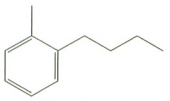
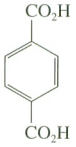
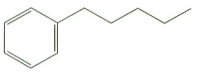
17.23 a)  b)  c)  d) 

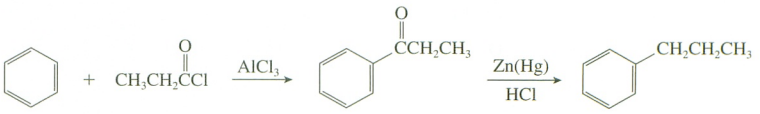
e)  f)  g)  h) 

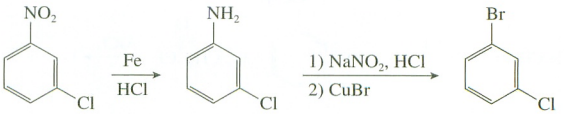
17.25 a)  b) 

17.26 a)  b)  c) 

17.27 a)  b)  c)  d) 

e)  f)  g) 

17.28 a) 

b) 

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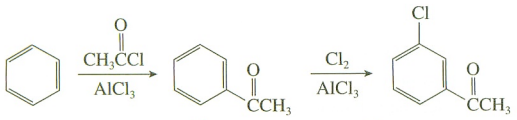

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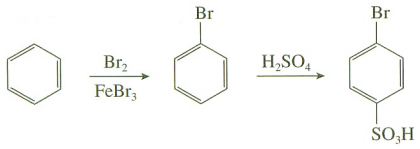

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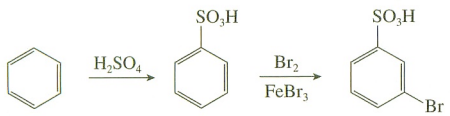

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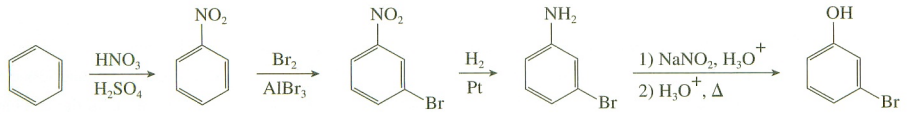

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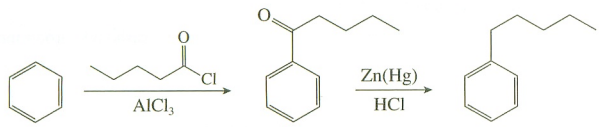

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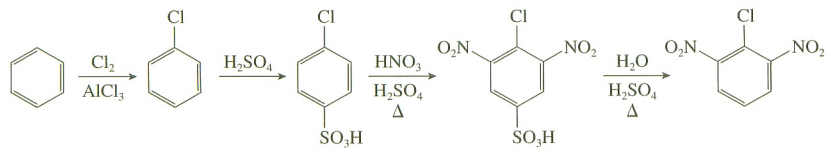

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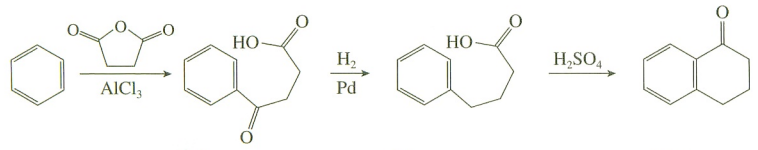

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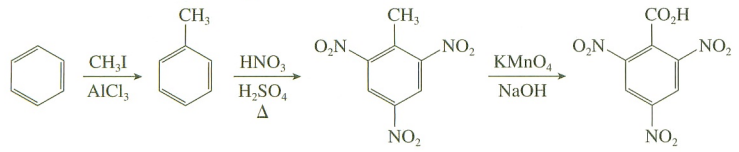
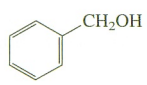


CHAPTER 18

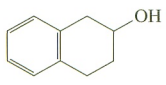
18.2 a)



b) $CH_3CH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_3$

c) $CH_3CH{=}CHCH_2CH_2\underset{\displaystyle OH}{\underset{|}{C}}H_2$

d)



18.4 a) Right compound due to inductive electron-withdrawing effect of F

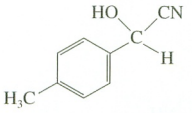
b) Right compound due to inductive and steric effects

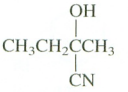
c) Left compound due to less steric hindrance

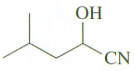
d) Right compound due to inductive electron-withdrawing effect of Cl

e) Not much difference because the steric effect is too far from the reacting carbonyl carbon

18.5 CH_3CH_2CH (Smallest K) < CH_2CH_2CH < CH_3CHCH < CH_3CF_2CH (Largest K)

18.6 a) 

b) 

c) 

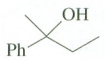
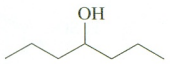
18.7 a) Right compound because aldehydes are less sterically hindered than ketones

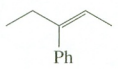
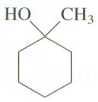
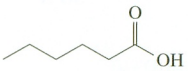
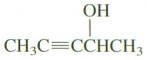
b) Left compound because resonance makes the carbonyl carbon of the right compound less electrophilic

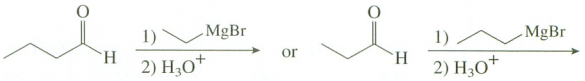
c) Left compound because the ethoxy group in right compound donates electrons to the carbonyl group by resonance, making the carbonyl carbon less electrophilic

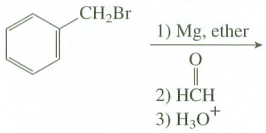
d) Right compound because the electron-withdrawing nitro group makes its carbonyl carbon more electrophilic

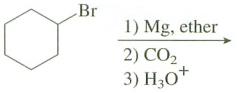
18.8 a) $CH_3CH_2CH_2CH_3$ b) c) $CH_3CH_2C{\equiv}CMgBr + CH_3CH_3$

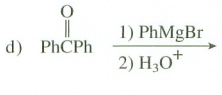
18.9 a)  b) c) 

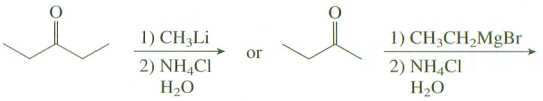
d)  e)  f)  g) 

18.10 a) 

b) 

c) 

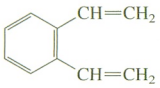
d) 

e) 

18.11 An acid–base reaction between the Grignard reagent and the hydroxy group on the aldehyde destroys the Grignard reagent.

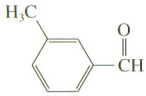
18.12 $Ph_3P + PhCH_2Cl \xrightarrow{S_N2} Ph_3\overset{+}{P}—CH_2Ph\ \overset{-}{Cl}$

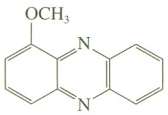
18.13 a) $PhCH{=}CHCH_2CH_3$ b) c) $HC{\equiv}CCH{=}CHCH_2CH_2CH_3$

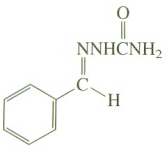
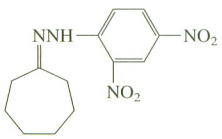
d)  e) $PhCH{=}CHCOEt$

18.14 The conjugate base (the ylide) is stabilized by resonance with the phenyl group.

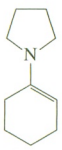
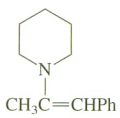
18.15 a) $PhCH_2CH \xrightarrow{Ph_3P^+-\bar{C}HCH_2CH_3}$ or $CH_3CH_2CH \xrightarrow{Ph_3P^+-\bar{C}HCH_2Ph}$

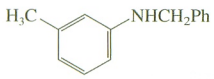
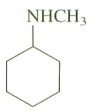
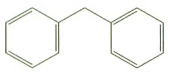
b) $CH_3CH_2CH \xrightarrow{Ph_3P^+-\bar{C}HCCH_2CH_3}$ c)  $\xrightarrow{Ph_3P^+-\bar{C}HCOCH_3}$

18.16 a) b)  c) $CH_3\overset{\overset{NOH}{\|}}{C}CH_2CH_3$

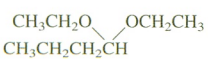
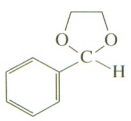
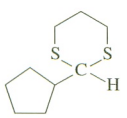
d)  e) 

18.18 Formation of the more stable conjugated enamine is preferred.

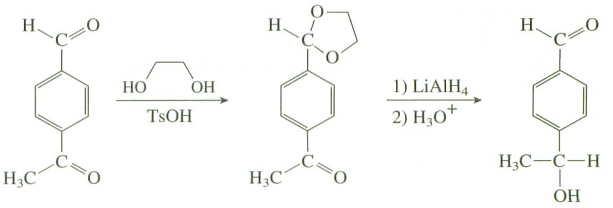
18.19 a)  b) 

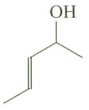
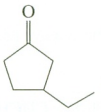
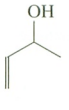
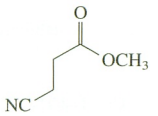
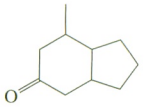
18.20 a)  b)  c) 

18.21 The right compound gives more cyclic hemiacetal at equilibrium because a five-membered ring is more stable than a four-membered ring.

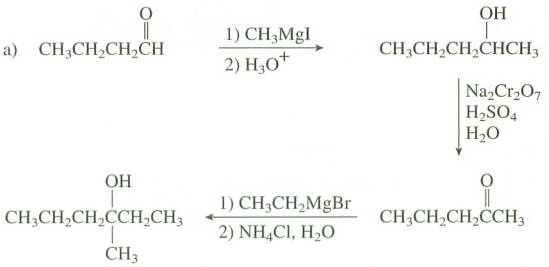
18.23 a)  b)  c) 

18.24



18.25 a)  b)  c)  d)  e) 

18.26 a)



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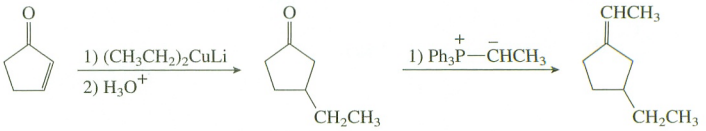


CHAPTER 19

19.1 a) Left ester due to less steric hindrance

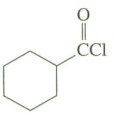
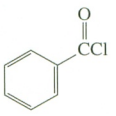
b) Left compound due to a more electrophilic carbonyl carbon because of the electron-withdrawing F

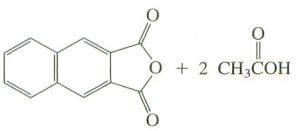
c) Left compound due to a more electrophilic carbonyl carbon because of the electron-withdrawing nitro group

19.2 a) Products b) Reactants c) Products

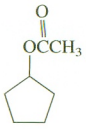
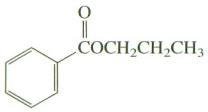
19.3 The reaction of the ester is faster because an ester is more reactive than an amide.

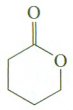
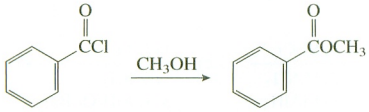
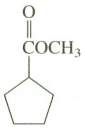
19.4 $CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}Cl + NH_2CH_2CH_2CH_3 \longrightarrow$

19.5 a)  b)  c) $CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}Cl$

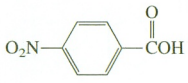
19.6 a) $CH_3CH_2\overset{\overset{O}{\|}}{C}O\overset{\overset{O}{\|}}{C}CH_2CH_3$ b) 

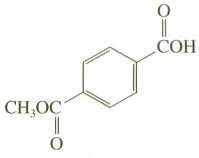
19.8 The reaction produces aspirin, an ester, rather than the more reactive anhydride.

19.9 a)  b)  c) $CH_3COCH_2CHCH_3$ (CH$_3$ branch) + CH_3COH

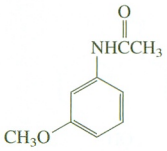
d)  e)  f) 

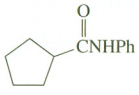
19.12 a) 2 CH_3COH b) $PhCO_2^-$ + $HOCH_2CH_3$ c) CH_3CO_2H + $PhNH_3^+ Cl^-$

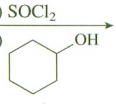
d)  e) CH_3CH_2COH + $HOCH_2CH_3$ f) $PhCCH_2CNH_2$

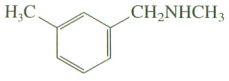
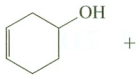
g) $CH_3CH_2CHCH_3$ (OH) h)  i) $CH_3CH_2CH_2COH$

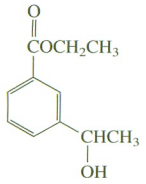
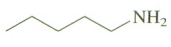
19.13 $PhCH_2Br \xrightarrow[DMSO]{NaCN} PhCH_2C{\equiv}N \xrightarrow[H_2O,\ reflux]{H_2SO_4} PhCH_2COH$

19.14 a)  b) $CH_3CH_2CH_2CN(CH_2CH_3)_2$

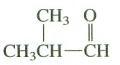
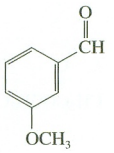
c)  d) $PhCNHCH_3$

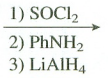
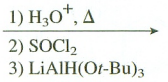
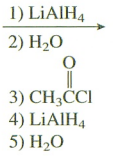
19.16 a) 1) $SOCl_2$, 2)  b) 1) $SOCl_2$, 2) excess $CH_3CH_2CH_2NH_2$ c) 1) H_3O^+, Δ, 2) $SOCl_2$, 3) CH_3CH_2OH

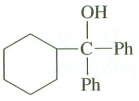
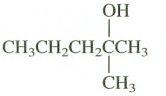
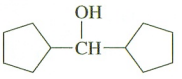
19.17 a) $CH_3CH_2CH_2CH_2OH$ + CH_3OH b)  c)  + CH_3CH_2OH

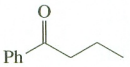
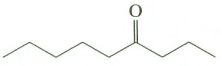
d)  e) 

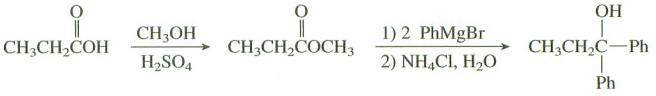
19.18 If acid were used, the product, an amine, would also be protonated.

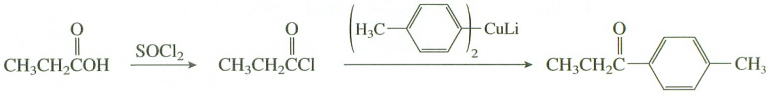
19.19 a)  b)  c)

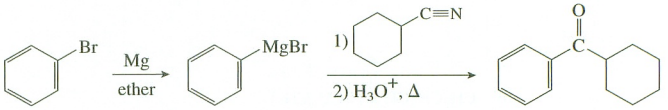
19.20 a) b)  c)  d) 

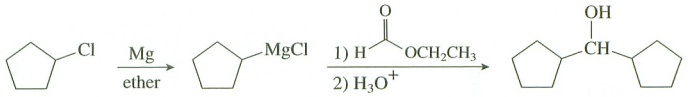
19.21 a)  b)  c) 

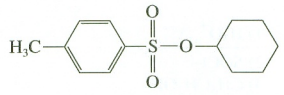
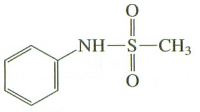
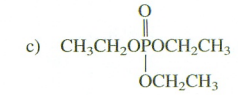
19.23 a)  b) 

19.24 a) 

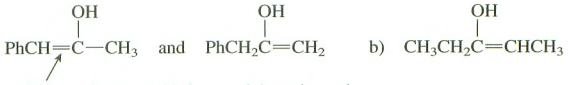
b) 

c) 

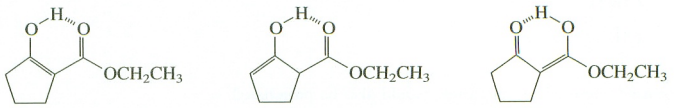
d) 

19.25 a)  b)  c) 

CHAPTER 20

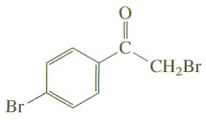
20.1 a) 

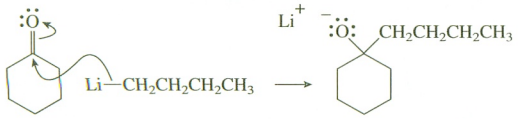
This one is more stable because it is conjugated.

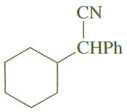
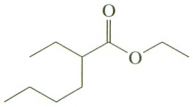
c) 

This one is more stable due to conjugation, hydrogen bonding, and loss of the ketone rather than the ester carbonyl group.

20.2 a) $PhC(=O)\ddot{C}HCH_3$ b) $CH_3CH_2C(=O)\ddot{C}HC(=O)OCH_2CH_3$ c) $Ph\ddot{C}HC(=O)CH_2CH_3$ d) $CH_3CH_2\ddot{C}HCN$

20.3 a)  b) $H_3C-C(CH_3)_2-C(=O)-OH + Br_3CH$

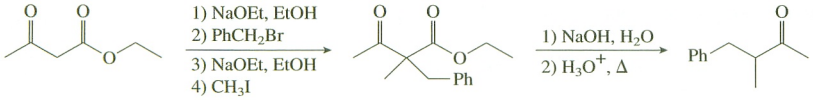
20.4 

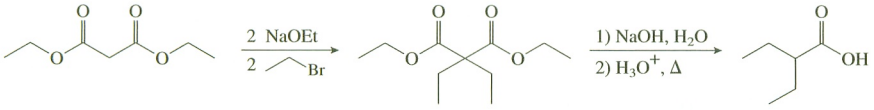
20.5 a)  b)  c) $PhC(=O)CH(CH_2CH_3)_2$

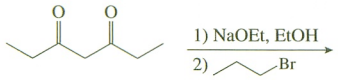
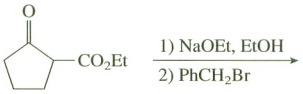
20.6 a) $CH_3C(=O)CH(CH_2Ph)C(=O)OEt$ → 1) NaOH, H_2O; 2) H_3O^+, Δ → $CH_3C(=O)CH_2CH_2Ph$

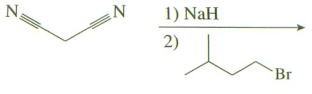
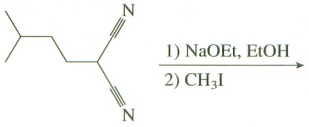
b) $EtOC(=O)CH(CH_2CH_2CH_3)C(=O)OEt$ → 1) NaOH, H_2O; 2) H_3O^+, Δ → $CH_3CH_2CH_2CH_2C(=O)OH$

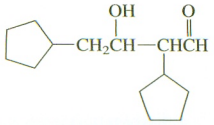
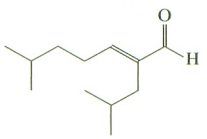
20.7 a) $EtOC(=O)CH_2C(=O)OEt$ → 1) NaOEt, EtOH; 2) $CH_3CHBrCH_3$ → $EtOC(=O)CH(CHCH_3CH_3)C(=O)OEt$ → 1) NaOH, H_2O; 2) H_3O^+, Δ → $CH_3CH(CH_3)CH_2CO_2H$

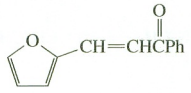
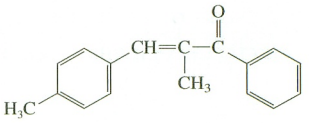
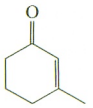
b) 

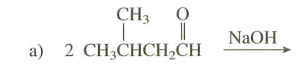
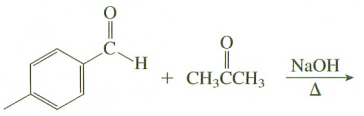
c) 

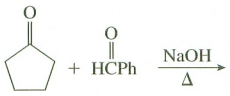
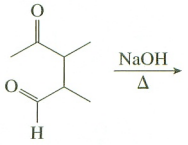
20.8 a)  b) 

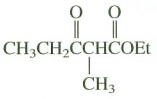
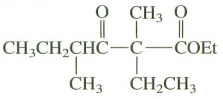
c)  d) 

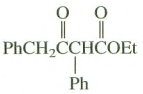
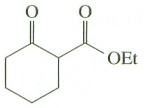
20.9 a)  b)  c) $PhCH_2CH{=}C(=O)CH$ (Ph)

20.11 a)  b)  c) 

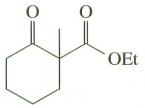
20.13 a)  b) 

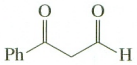
c)  d) 

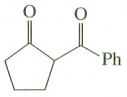
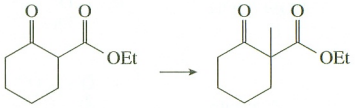
20.14 a)  b) 

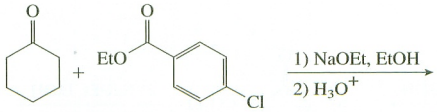
c)  d) 

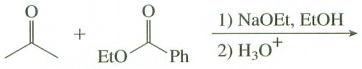
20.15 This product does not form because there is no acidic H between the two carbonyl groups, so the equilibrium driving step cannot occur.

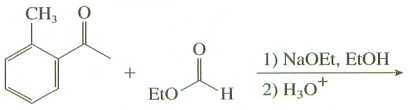


20.16 a) b) 

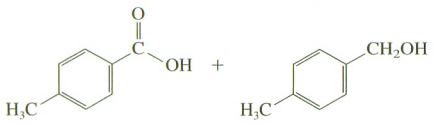
c)  d) 

20.18 a) 

b) 

c) 

20.20



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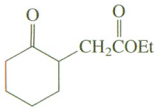

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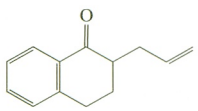

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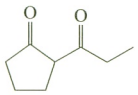

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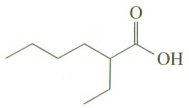

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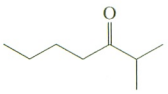
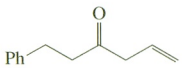
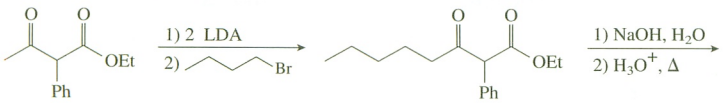


c) $CH_3CH_2CH_2CCH_2COCH_3$

d)



20.24 a)



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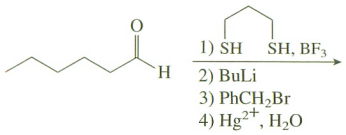

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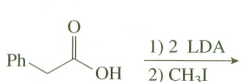
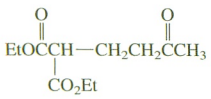


20.25 a)



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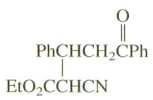

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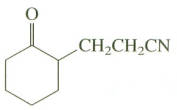
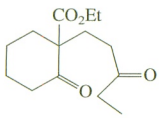
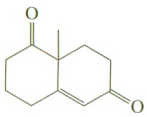


20.26 The hydrogen on the α-carbon bonded to the phenyl group is more acidic because the resulting enolate anion is stabilized by resonance with the phenyl group.

20.27

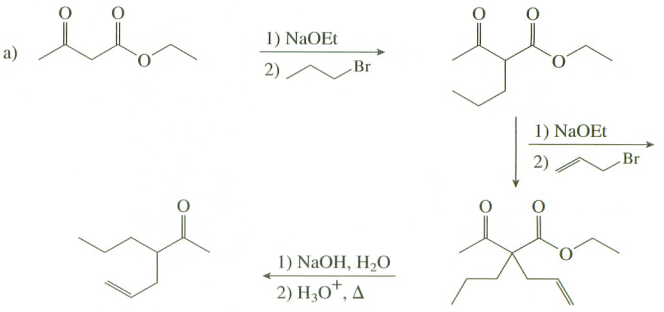


20.28



20.29

a)



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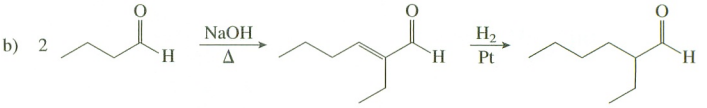
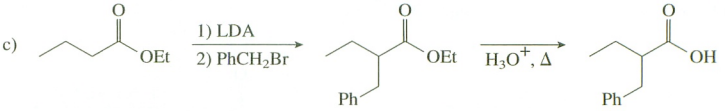
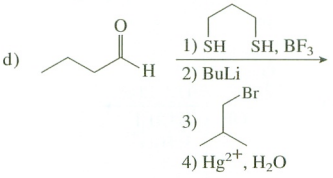


c)



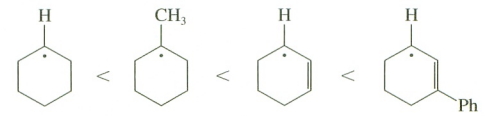
d)



CHAPTER 21

21.1

21.2



Least stable Most stable

21.3

a) + N_2

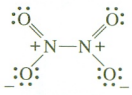
b) $2\ :\dot{\underset{\cdot\cdot}{\overset{\cdot\cdot}{Br}}}\cdot$

c) $2\ CH_3\underset{|}{\overset{CH_3}{CH}}-\ddot{O}\cdot$

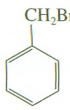
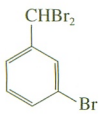
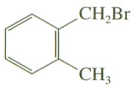
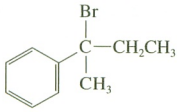
21.4 a) Abstraction of a tertiary hydrogen occurs more readily than abstraction of a secondary hydrogen, so the second reaction is faster.

b) Formation of the resonance stabilized benzylic radical occurs more readily, so the first reaction is faster.

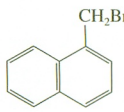
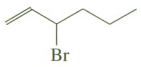
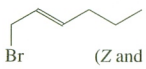
21.5 a) $CH_3\dot{C}HCH_2Br$ b) 2 $CH_3\overset{\overset{O}{\|}}{C}\ddot{O}\cdot$ c) $CH_3(CH_2)_6CH_3 + CH_3CH_2CH_2CH_3 + CH_3CH_2CH{=}CH_2$

d)  e) 2 $CH_3\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}\cdot + N_2$

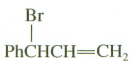
21.7 If the strength of a typical CH bond is taken as 98 kcal/mol (410 kJ/mol) (see Table 2.1), then the abstraction of the hydrogen atom by a fluorine atom is exothermic by 135 − 98 = 37 kcal/mol (155 kJ/mol), whereas a similar abstraction by an iodine atom is endothermic by 98 − 71 = 27 kcal/mol (113 kJ/mol).

21.8 a)  b)  c)  d) 

Racemic

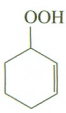
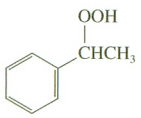
e)  f)  +  (*Z* and *E*)

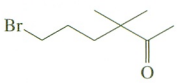
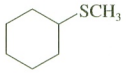
21.9 The major product is 1-phenyl-3-bromopropene because it is more stable due to conjugation.

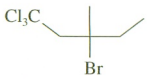
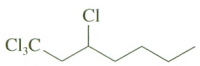


21.10 a) b) $PhCH_2CH_3$

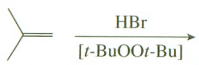
21.11 The radical is stabilized by resonance and its reactions are also slowed by steric hindrance.

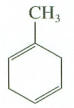
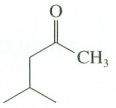
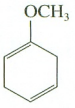
21.12 a)  b) 

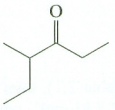
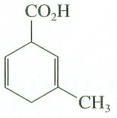
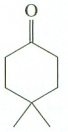
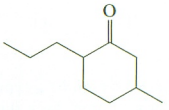
21.14 a) b)  c) d) 

e)  f) 

21.15 a) b) c)

d)  e) $PhCH{=}CH_2 \xrightarrow[[t\text{-BuOO}t\text{-Bu}]]{HBr}$

21.16 a)  b)  c)  d)

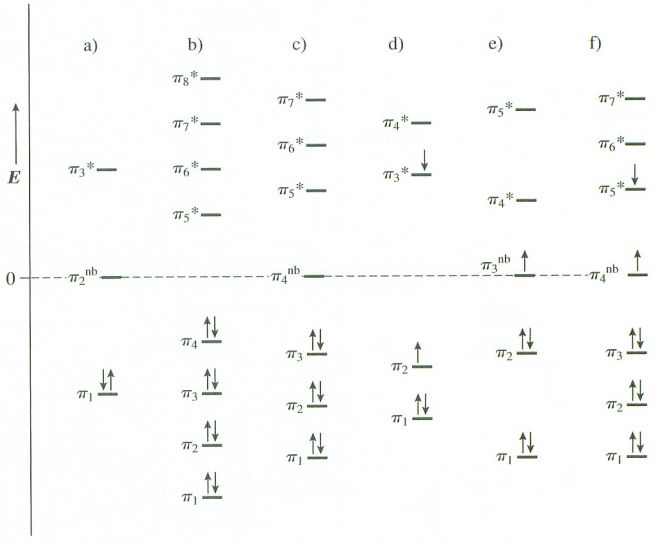
e)  f)  g)  h) 

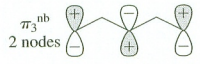
21.17 a) 1) Li, NH_3 (*l*); 2) $PhCH_2Br$ b) 1) Li, NH_3 (*l*); 2) H_3O^+

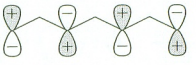
CHAPTER 22

22.1 a) Conrotation b) Disrotation

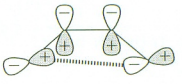
22.2



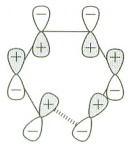
22.3 a)  b)

c) d)  e)

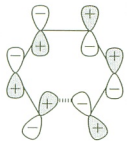
22.4 For the photochemical reaction the HOMO = π_3^*; conrotation is forbidden.



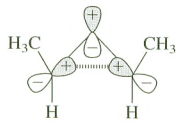
22.5 For the thermal reaction the HOMO = π_3; conrotation is forbidden.



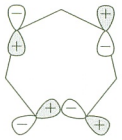
For the photochemical reaction the HOMO = π_4^*; disrotation is forbidden.



22.6 a) For the thermal reaction the HOMO = π_1; disrotation is allowed.



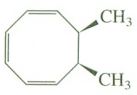
b) For the photochemical reaction the HOMO = π_4^{nb}; disrotation is forbidden.



22.7 a) For an odd number of electron pairs (1), disrotation is thermally allowed.
b) For an odd number of electron pairs (3), disrotation is photochemically forbidden.

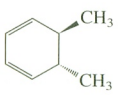
22.8 a) 2 electron pairs; disrotation; photochemically allowed
b) 3 electron pairs; conrotation; thermally forbidden
c) 2 electron pairs; disrotation; thermally forbidden
d) 4 electron pairs; disrotation; photochemically allowed

22.9 a)

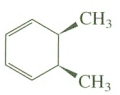


b)

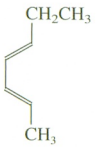
c)



d)

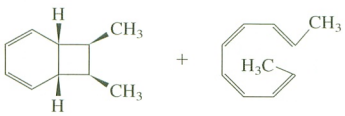


e)

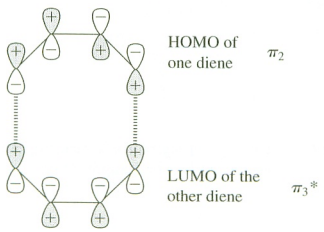


f)

g)

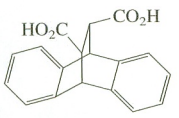
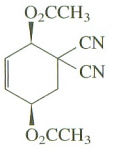
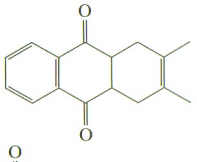


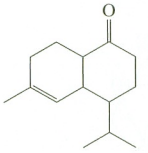
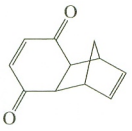
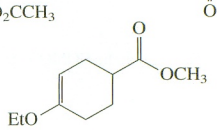
22.11 One overlap is bonding and the other is antibonding, so the reaction is forbidden.

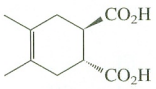
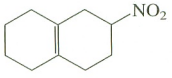
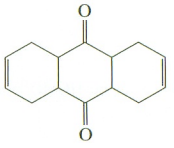
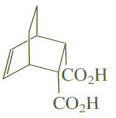


22.12 a) A [4 + 4] cycloaddition involves 4 electron pairs and is photochemically allowed.
b) A [6 + 2] cycloaddition involves 4 electron pairs and is photochemically allowed and thermally forbidden.

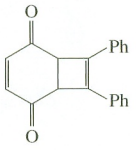
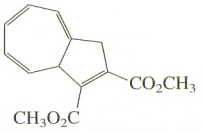
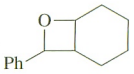
22.13 The left diene is more reactive because its *s*-cis conformation is less hindered and is therefore present in higher concentration.

22.14 a) b)  c)  d) 

e)  f)  g) 

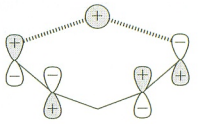
h)  i)  j)  k) 

22.15 [10 + 2] cycloaddition; 6 electron pairs; photochemically allowed

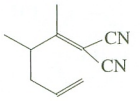
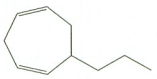
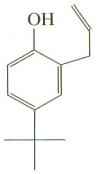
22.16 a) b)  c)  d) 

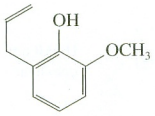
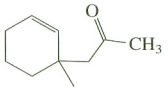
22.17 a) [3,3] Sigmatropic rearrangement b) [1,7] Sigmatropic rearrangement
c) [3,5] Sigmatropic rearrangement

22.18 Use π_4^* of the pentadienyl radical. One overlap is bonding and one is antibonding, so the reaction is forbidden.

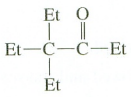
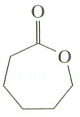
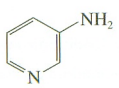


22.20 a) Thermally allowed b) Photochemically allowed c) Photochemically allowed

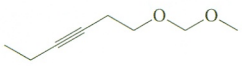
22.21 a)  b)  c) 

d)  e) 

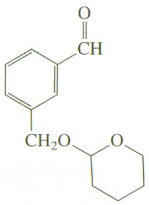
22.22 It is a [3,3] sigmatropic rearrangement and is thermally allowed. The reactant is favored at equilibrium because it has less angle strain.

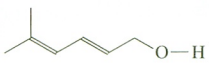
22.23 a)  b) c)  d) 

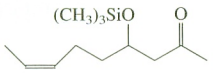
CHAPTER 23

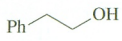
23.1 a) 

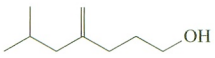
b) $PhCH_3$ +

c) 

d) 

e) 

f) 

g) 

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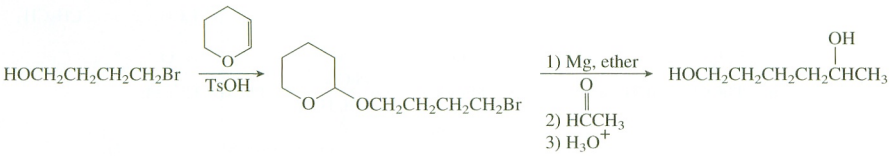
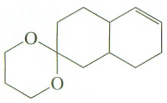
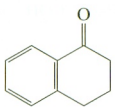
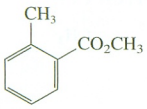
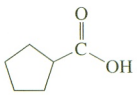
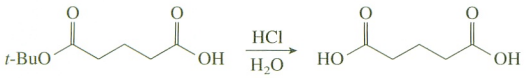


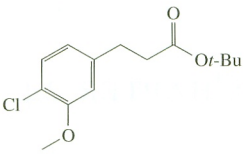
23.4 a) 

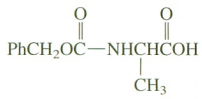
b) 

23.5 a) 

b) 

c) 

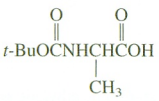
d) 

23.7 a) 

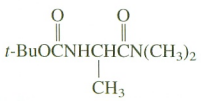
b)

c) $PhCH_3 + NH_2CH_2CH_2Ph + CO_2$

d)

23.8 

A



B

The amide cannot be prepared directly because the unprotected amino group will react with the acyl chloride group.

23.9 The ester bond of the carbamate group is hydrolyzed more rapidly than either amide bond. The resulting carbamic acid then eliminates carbon dioxide to produce the amine. Conditions drastic enough to hydrolyze an amide bond are never employed in this process.

23.10 a) $CH_3CH_2CH_2\overset{OH}{\overset{|}{C}}HCH_2CHCH_3$ (with CH_3) $\Longrightarrow$ $CH_3CH_2CH_2^-$ + $^+CHCH_2CHCH_3$ (OH, CH_3)

1) $CH_3CH_2CH_2MgBr$ 2) H_3O^+ → $HCCH_2CHCH_3$ (O, CH_3)

23.11 a) $HC{\equiv}CH \xrightarrow[2)\ CH_3CH_2Br]{1)\ NaNH_2} CH_3CH_2C{\equiv}CH \xrightarrow[2)\ CH_3CH_2Br]{1)\ NaNH_2} CH_3CH_2C{\equiv}CCH_2CH_3$

Lindlar catalyst, H_2 → CH_3CH_2(H)C=C(H)CH_2CH_3

b) $PhCCl$ (O) + $(CH_3)_2CuLi$ → $PhCCH_3$ (O) $\xrightarrow[NaOH,\ H_2O,\ \Delta]{PhCH\ (O)}$ $PhCH{=}CHCPh$ (O)

c) $PhCH_2Br \xrightarrow[DMSO]{KCN} PhCH_2CN \xrightarrow[\Delta]{H_3O^+} PhCH_2COH$ (O) $\xrightarrow[H_2SO_4]{CH_3OH} PhCH_2COCH_3$ (O)

1) 2 CH_3MgI 2) NH_4Cl, H_2O → $PhCH_2\overset{OH}{\overset{|}{C}}CH_3$ (CH_3)

CHAPTER 24

24.2 a) $-(CH_2-\overset{Cl}{\overset{|}{C}}H)_n-$ b) $-(CH_2-\overset{CN}{\overset{|}{C}}H)_n-$ c) $-(CH_2-\overset{Cl}{\overset{|}{\underset{Cl}{\overset{|}{C}}}})_n-$

24.3 a) $CH_2{=}\overset{OCCH_3\ (O)}{\overset{|}{C}}H$ b) $F_2C{=}CF_2$

24.5 Both (a) and (b) can form atactic polymers, whereas (c) cannot.

24.6 The primary carbocation that is required as an intermediate in the cationic polymerization of ethylene is too unstable.

24.7 The anionic intermediate formed in the polymerization of acrylonitrile is stabilized by resonance and is readily formed, whereas the anionic intermediate formed in the polymerization of isobutylene is quite unstable and is difficult to form.

24.8 THF is much less reactive toward nucleophiles than is ethylene oxide because no ring strain is relieved when THF reacts.

24.9 a) The alkene on the right produces a more crystalline polymer because it has no chirality centers and is more stereoregular.

b) The alkene on the right produces a more crystalline polymer because its side chain is more polar.

c) Coordination polymerization produces a less branched and more stereoregular polymer that is more crystalline.

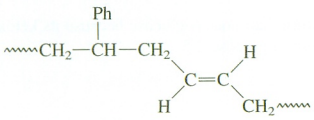
d) The alkene on the right produces a more crystalline polymer because it has no chirality centers and is more stereoregular.

24.10 Teflon has no chirality centers, so it has no stereochemical complications; nor does it have any hydrogens that can be abstracted from the interior of the chain, so it is linear.

24.11 Poly(methyl methacrylate) cannot be prepared by cationic polymerization because the carbonyl group destabilizes the intermediate carbocation. It can be produced by anionic polymerization because the carbonyl group stabilizes the carbanion intermediate by resonance.

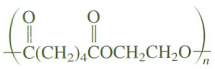
24.12 Radicals prefer to add to C-1 of isoprene because the resulting radical is the most stable of the four possibilities. It is stabilized by resonance, and the odd electron is on a tertiary carbon in one resonance structure and a primary carbon in the other. In contrast, addition at C-2 or C-3 produces less stable radicals because they have no resonance stabilization. Addition at C-4 produces a resonance stabilized radical, but the odd electron is on a secondary carbon and a primary carbon in the two resonance structures.

24.13

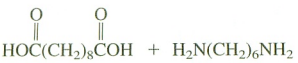


Trans double bonds predominate because they are more stable than cis double bonds.

24.14



24.15

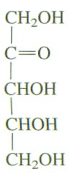


24.16 If the polyester is to be formed from more diol units, then each polymer chain must terminate with a diol unit at each end. To accommodate even a small excess of diol units, there must be many chains, so the chains must be relatively short.

24.17 Direct preparation of poly(vinyl alcohol) would require an enol as the monomer. However, recall from Section 11.6 that most enols cannot be isolated because they spontaneously isomerize to the carbonyl tautomer.

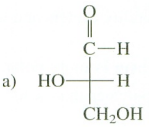
CHAPTER 25

25.1

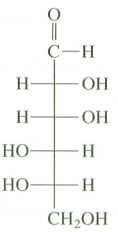


25.2 Eight aldopentoses; four 2-ketopentoses

25.3 a)

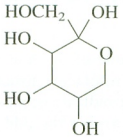


b)

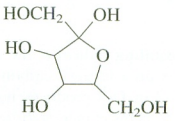


25.4 a) L-Erythrose b) L-Gulose c) D-Altrose

25.6



Pyranose

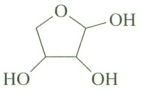


Furanose

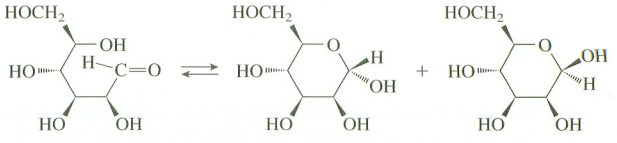
D-Fructose has more of its uncyclized form present at equilibrium than does D-glucose because its ketone carbonyl group is less reactive than the aldehyde carbonyl group of glucose.

25.7 Identical to D-glucose

25.8

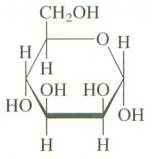


25.9

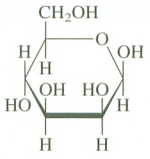


α-D-Mannopyranose β-D-Mannopyranose

25.10

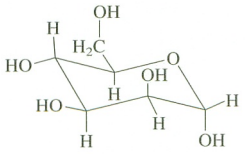


α-D-Mannopyranose

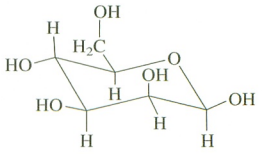


β-D-Mannopyranose

25.11



α-D-Mannopyranose



β-D-Mannopyranose

25.12 67.4% α, 32.6% β

25.13 Galactaric acid is a meso compound.

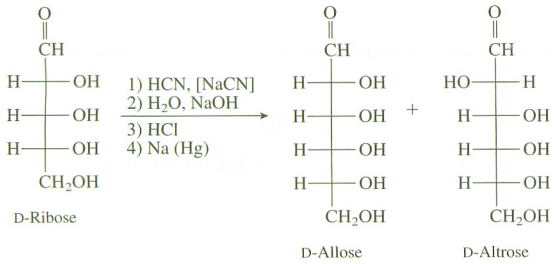
25.14 D-Ribose and D-xylose

25.15 Xylitol is a meso compound.

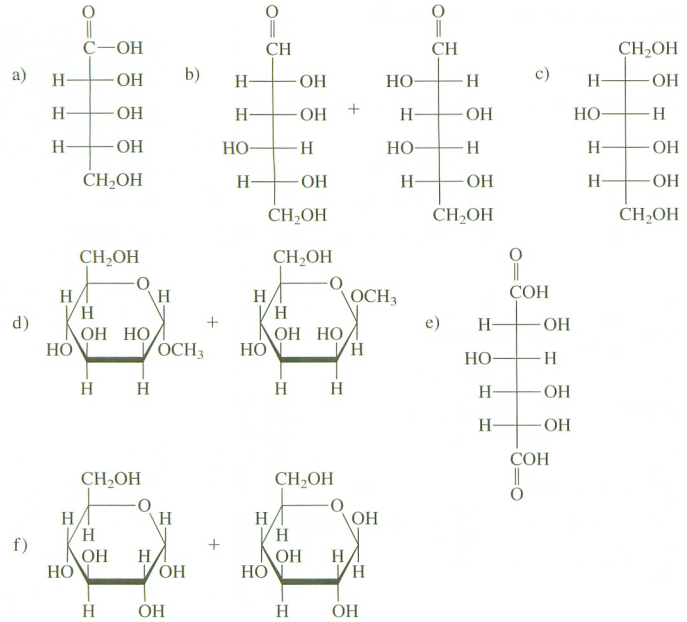
25.16 D-Allose and D-galactose

25.17 Under these reaction conditions, α-D-glucopyranose undergoes isomerization to the β-isomer.

25.20

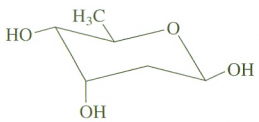


25.21



25.24 Maltose and cellobiose both have a hemiacetal group that is in equilibrium with an aldehyde group in aqueous solution. It is the aldehyde group that gives a positive test for a reducing sugar. Sucrose does not have a hemiacetal group, so there is no aldehyde group present at equilibrium in a solution of sucrose.

25.25



There are no hydroxy groups present on C-2 and C-6.

CHAPTER 26

26.1 Isoleucine and threonine

26.2 The positively charged nitrogen acts as an inductive electron-withdrawing group and therefore makes the carboxylic acid group a stronger acid.

26.3 The ester is the stronger acid because the inductive electron-withdrawing effect of the ester group increases the acid strength of the ammonium group. The carboxylate anion is an electron-donating group and decreases the acid strength of the ammonium group in the amino acid.

26.4 The inductive electron-withdrawing effect of the positively charged nitrogen, which increases acid strength, is stronger at the main carboxylic acid group because the distance separating the groups is smaller. Inductive effects decrease rapidly with distance.

26.5 The carboxylic acid group in the side chain of glutamic acid is farther from the electron-withdrawing positive nitrogen than is the case with aspartic acid.

26.6 a) b) $^{-}S-CH_2CH(^{+}NH_3)-CO_2^{-}$ c) $H_2N^{+}=C(NH_2)NHCH_2CH_2CH_2CH(^{+}NH_3)CO_2^{-}$

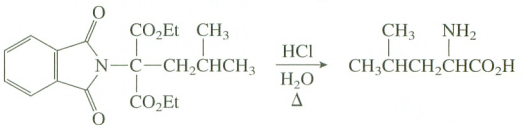
26.7 a) $H_3N^{+}CH_2CH_2CH_2CH_2CH(^{+}NH_3)CO_2H$ $H_3N^{+}CH_2CH_2CH_2CH_2CH(^{+}NH_3)CO_2^{-}$

$H_3N^{+}CH_2CH_2CH_2CH_2CH(NH_2)CO_2^{-}$ $H_2NCH_2CH_2CH_2CH_2CH(NH_2)CO_2^{-}$

26.8 a) Cl^{-} $NH_3^{+}CH(CH_3)COCH_2Ph$ b) $PhC(=O)NHCH(CH_2CHCH_3)C(=O)OH$ c) $CH_3C(=O)NHCH(CH_3)C(=O)OH$

26.10 a) $PhCH_2CH(NH_2)CN \xrightarrow[H_2O]{HCl} PhCH_2CH(NH_2)CO_2H$

b) $CH_3CH(Br)CH(CH_3)C(=O)OH \xrightarrow[NH_3]{\text{excess}} CH_3CH(NH_2)CH(CH_3)C(=O)OH$

c) 

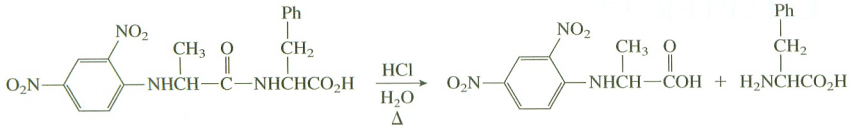
26.11 a) $CH_3CH(CH_3)CH_2CH=O \xrightarrow[2)\ HCl,\ H_2O]{1)\ NaCN,\ NH_4Cl,\ H_2O} CH_3CH(NH_2)CH(CH_3)CO_2H$

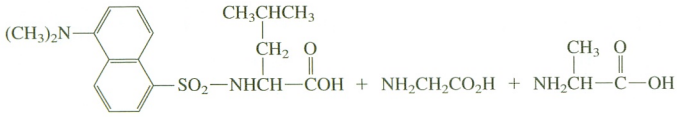
b) $PhCH_2CH_2C(=O)OH \xrightarrow[2)\ \text{excess } NH_3]{1)\ Br_2,\ [PBr_3]} PhCH_2CH(NH_2)C(=O)OH$

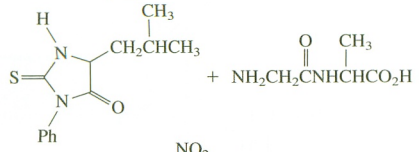
26.13 $NH_2CH(CH_2Ph)C(=O)NHCH(CH_3)C(=O)NHCH(CH_2CO_2H)C(=O)OH$

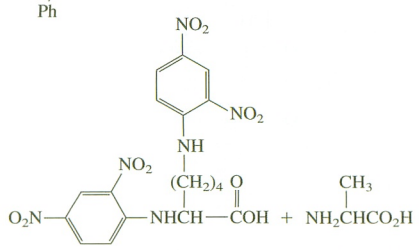
26.14 Leu-Cys-Tyr-Glu

26.15 The amide groups in the side chains of asparagine and glutamine residues in a peptide are cleaved under the same conditions that hydrolyze the amide bonds of the peptide. Therefore, aspartic acid and glutamic acid are isolated instead.

26.17 a) 

b) 

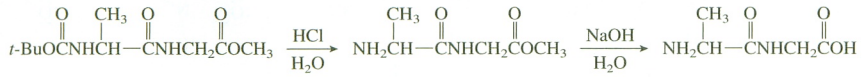
c) 

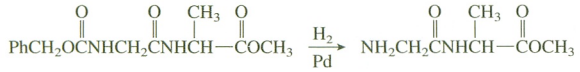
d) 

26.18 Phe-Phe-Ala or Phe-Ala-Phe

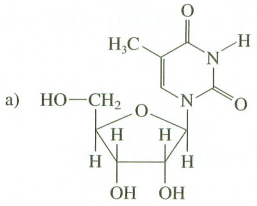
26.21 a)

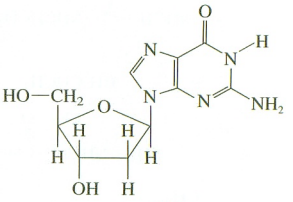
b)

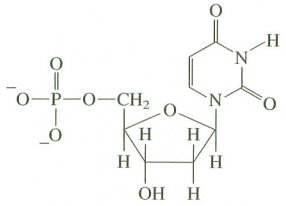
c) 

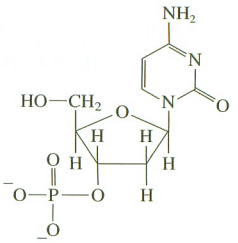
d) 

CHAPTER 27

27.1 a) 

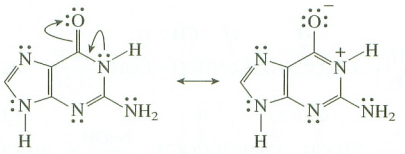
b) 

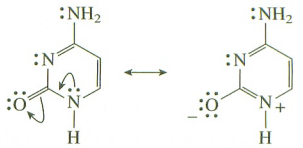
c) 

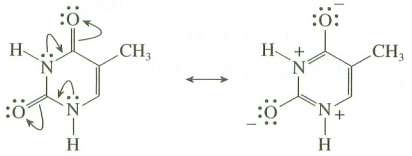
d) 

27.2 a) Guanosine b) Uridine 5'-monophosphate
c) Deoxycytidine 5'-monophosphate

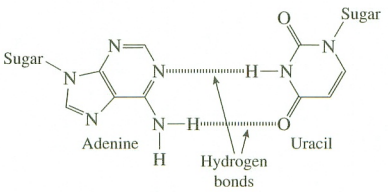
27.3 Pyrimidine has six electrons in its cyclic pi system and therefore fits Huckel's rule. The unshared electrons on the nitrogens are not part of the pi system. The six-membered ring of purine is aromatic for the same reason as pyrimidine. The five-membered ring is also aromatic. Like imidazole (see Chapter 16), it has a total of six electrons in its cyclic pi system. The electrons on N-9 are part of the pi system, whereas the electrons on N-7 are not.

27.4 a) 

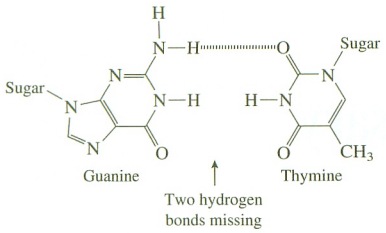
b) 

c) 

27.5 5' end TAACGCTCG 3' end

27.6 

27.7



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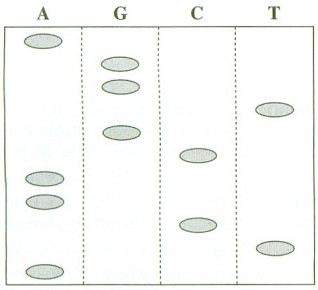
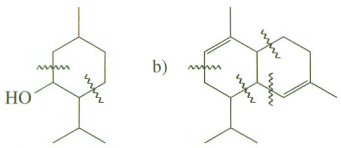
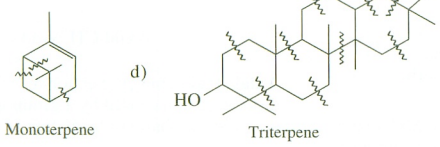


CHAPTER 28

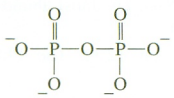
28.1 a) b)



c) d)



28.4



This is a good leaving group because it is a weak base.

28.7 The cyclization occurs so as to form the more stable tertiary carbocation.

28.8 Path A is disfavored because it produces a secondary carbocation. It is favored because the five-membered rings that are formed have lower ring strain. Path B is favored because it produces a tertiary carbocation. It is disfavored due to the strain in the four-membered ring of the product.

28.9 The cyclization occurs so as to form the more stable tertiary carbocation.

28.11 Both cyclizations occur so as to form the more stable tertiary carbocations.

28.16 The epoxide opens so as to form the more stable tertiary carbocation.